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ON THE PROPYL DERIVATIVES AND DECOMPOSITION PRODUCTS OF ETHYL ACETOACETATE.[1]

BY BEVERLY S. BURTON.

Preparation of Monopropylethyl Acetoacetate.

This was prepared according to the modified process of Conrad and Limpach.[2] 27 grams of sodium were dissolved in 270 grams of absolute alcohol, then 152.7 grams of ethylacetoacetate were added, and gradually 206 grams of propyliodide. This mixture was then heated for several hours on the water-bath with an inverted condenser until it was perfectly neutral. The alcohol was then distilled off, and a sufficient quantity of water added to dissolve the separated sodium iodide. The oily liquid product thus formed was then, in a separating funnel, separated from the aqueous solution, the former was washed with water, dried with calcium chloride and subjected to repeated fractional distillation. In this manner 117 grams of a clear, limpid liquid, boiling between 205° and 210°, of a pleasant ethereal odor, were obtained. By far the greatest portion distilled between 208° and 209°. Its specific gravity was 0.981 at 0°, compared with water at 4°. The combustion gave the following results:

[1] From the author's Dissertation, Würzburg, 1881.

[2] Ann. Chem. Pharm. **192**, 153.

I. 0.2554 gram substance yielded 0.5839 gram CO_2 and 0.2192 gram H_2O.

II. 0.1761 gram substance yielded 0.4052 gram CO_2 and 0.1526 gram H_2O.

	Calculated.	Found. I.	Found. II.
C_9	62.79	62.35	62.75
H_{16}	9.30	9.57	9.63
O_3	27.91	...	...
	100.00		

Corresponding to the formula of monopropylethyl-acetoacetate $\begin{cases} CH_3 \\ CO \\ CH(C_3H_7) \\ CO.OC_2H_5. \end{cases}$

Preparation of Dipropylethyl Acetoacetate.

The method of preparation in this instance was in every respect similar in principle to that employed and above described, with the exception that here the monopropylethyl acetoacetate was used instead of ethylacetoacetate. 27 grams of sodium were dissolved in 270 grams of absolute alcohol as before; 202.2 grams monopropylethyl acetoacetate added, then 200 grams of propyliodide. Out of the separated oily liquid, 119 grams, boiling between 235° and 236°, were obtained by fractional distillation.

The analyses yielded the following results:

I. 0.1978 gram substance 0.1876 gram H_2O; 0.4866 gram CO_2.

II. 0.1377 gram substance 0.1292 gram H_2O; 0.3377 gram CO_2.

	Calculated.	Found. I.	Found. II.
C_{12}	67.29	67.09	66.88
H_{22}	10.28	10.54	10.42
O_3	22.43	...	...
	100.00		

From which is calculated the formula $\begin{cases} CH_3 \\ CO \\ C(C_3H_7)_2 \\ CO.OC_2H_5 \end{cases}$. The dipropylethyl acetoacetate is very similar to the monopropyl substitution product. It is a coloress, limpid liquid, of pleasant odor, boiling

point 235–236°. Specific gravity 0.9585 at 0°, compared with water at 4°.

Saponification of Mono- and Dipropylethyl Acetoacetate.

It was first shown by Geuther[1] in 1865 that ethylacetoacetate when subjected to the action of alkalies, undergoes decomposition, and yields acetone, carbon dioxide and alcohol. Later the researches of Frankland and Duppa[2] proved that this decomposition held true not only for ethylacetoacetate, but for all alkyl derivatives of the same, expressed by the following equation:

$$\begin{matrix}CH_3\\CO\\C(XY)\\CO.OC_2H_5\end{matrix} + 2KOH = \begin{matrix}CH_3\\CO\\C(XY)H\end{matrix} + K_2CO_3 + C_2H_5.OH.$$

Wislicenus[3] now showed that at the same time with this above mentioned, there occurs a second decomposition, by which acetic acid is always formed, or in case an alkyl substitution product is subjected to the reaction, an alkyl substituted acetic acid is also formed in accordance with the following equation:

$$\begin{matrix}CH_3\\CO\\C(XY)\\COOC_2H_5\end{matrix} + 2KOH = \begin{matrix}CH_3\\COOK\end{matrix} + \begin{matrix}C(XY)H\\COOK\end{matrix} + C_2H_5.OH.$$

He found that the relative amounts of ketone and organic acid that are formed are dependent not only upon the substituted radical, but also upon the concentration of the alkali employed. In the method for the quantitative saponification[4] is established, that the amount of ether which is split up into two molecules of organic acids is greater the more concentrated the employed alkali, and the more concentrated the alkali remains after the saponification is effected. On the contrary, the more carbondioxide and ketone are formed the more dilute the employed alkali is.

The following experiments were made according to the above mentioned method of Wislicenus. Monopropylethyl acetoacetate boiling between 208°–209°, and dipropylethyl acetoacetate boiling at 235.5°, were employed.

[1] Jahresbricht, 1865, 302.
[2] Ann. Chem. **135**, 217.
[3] Ann. Chem. **186**, 161.
[4] Ann. Chem. **190**, 257–281.

Observations.

	10 cc. KOH sol. = cc. HCl.	10 cc. HCl = 0.0351 gr. HCl.	Emplo'd		Diluted to 100 cc. 10 cc. yielded			require	TOTAL.			
			Ether.	Potash.	CO_2	t°	Bar	HCl	CO_2	Ether decomp. in Organic Salts.	Ether decomp. in Ketone and CO_2	KOH in Organic Salts.
	cc.		gr.	cc.	cc.		mm	cc.	gr.	gr.	gr.	gr.
Propylethyl acetoacetate with 10 per cent. KOH sol.	18.70		1.72	17	17.26	11.8	747	2.64	0.3198	0.4434	1.2502	0.2802
" 20 " " " I	36.50		1.72	9	13.05	10.	745	2.36	0.2427	0.7639	0.9487	0.4983
" 20 " " " II	36.50		1.72	9	11.76	9.4	745	2.29	0.2192	0.8230	0.8567	0.5372
Dipropylethyl acetoacetate with 10 per cent. KOH sol. I	18.38		2.14	17	8.30	15.	741	1.91	0.1509	1.2516	0.7337	0.6562
" 10 " " " II	18.38		2.14	17	8.77	15.	741	1.94	0.1595	1.2646	0.7759	0.6630
" 20 " " "	37.25		2.14	9	2.96	16.5	745	1.55	0.0538	1.8588	0.2617	0.9743

From which is calculated—

	Concentration of the potash sol. Begin.	End.	Employed to 1 mol. ether molec. KOH.	Decomp. of ether in Organic Salts.	Ketone and CO_2	Total.
Propylethyl acetoacetate with 10 per cent. KOH sol.	10.09	1.43	3.06	25.78	71.68	97.46
" 20 " " " I	19.69	1.27	3.16	44.41	55.16	99.57
" 20 " " " II	19.69	1.23	3.16	47.88	49.81	97.69
Dipropylethyl acetoacetate with 10 per cent. KOH sol. I	9.91	1.03	3.00	58.49	34.29	92.78
" 10 " " " II	9.91	1.02	3.00	59.09	36.26	95.35
" 20 " " "	20.10	0.83	3.22	86.84	12.23	99.07

The following table offers a convenient comparison of the decomposition products of the mono- and dipropylethyl acetoacetates with those of the methyl and ethyl derivatives as given by Wislicenus.[1]

With 10 per cent. KOH sol.	Methyl.	Ethyl.	Propyl.	Dimethyl.	Diethyl.	Dipropyl.
Ketone and CO_2	86.28	91.52	71.68	91.73	54.15	34.24
Organic Salts	13.70	8.75	25.78	7.46	42.50	58.78
With 20 per cent. KOH sol.						
Ketone and CO_2	68.16	75.44	55.16	80.02	30.86	12.22
Organic Salts	31.20	23.75	44.41	19.96	69.46	86.69

From the above it is seen that monopropylethyl acetoacetate with both dilute and concentrated potash solution undergoes a decomposition by which ketone and carbon dioxide preponderate,

[1] Ann. Chem. **190**, 280.

which behavior is analogous to that of the other mono derivatives. Dipropylethyl acetoacetate, on the contrary, yields by decomposition with both dilute and concentrated alkali in a greater degree than the diethylethyl acetoacetate, principally organic salts, which behavior is especially marked when compared with the methyl derivative.

Dipropylacetic Acid.

Since it is established by the experiments just described that, by the decomposition of dipropylethyl acetoacetate with alkalies, principally organic acids are obtained, this circumstance was, therefore, taken advantage of for the preparation of dipropylacetic acid. 20 grams of dipropylethyl acetoacetate were treated on the water bath with 201 cc. of a 15 per cent. alcoholic solution of potash, with inverted condenser, and warmed for several hours. After dilution with water, the oily layer of ketone was separated, the aqueous alkaline solution was neutralized with sulphuric acid and evaporated to dryness; out of the dry residue the sodium salt of the organic acid was extracted with absolute alcohol, and in this manner purified. It forms a colorless, deliquescent mass. All attempts to obtain it in crystals were unsuccessful. By the addition of sulphuric acid to the salt the free acid was obtained, which was then dried and fractionally distilled.

The analysis yielded results in accordance with the anticipated formula $(C_3H_7)_2CH.CO.OH$.

I. 0.1238 gram acid gave 0.1269 gram H_2O; 0.3008 gram CO_2.
II. 0.1253 gram " 0.1273 gram H_2O; 0.3042 gram CO_2.

	Calculated.	Found.	
		I.	II.
C_8	66.67	66.26	66.21
H_{16}	11.11	11.39	11.29
O_2	22.22	...	...
	100.00		

Dipropylacetic acid is a colorless, oily liquid, with a slightly acid reaction, difficultly soluble in water, and possessing the characteristic odor of the higher fatty acids. Its specific gravity is $0.921\frac{5}{5}$ at 0°, compared with water at 4°. It boils at 219.5°.

Silver nitrate, copper sulphate and lead acetate give with the sodium salt precipitates. The barium salt is easily soluble. The

isomeric caprylic acid, which is a solid at ordinary temperature, boils at 232°, and forms a difficultly soluble barium salt.

Ethyl Ether.—The ether was prepared by decomposition of the silver salt (11 grams) with ethyl iodide (6.21 grams). The reaction came to an end in a short time upon the water-bath. The ether was then extracted with ordinary ether, which was distilled off. The remainder was then fractionally distilled, and the following result obtained by the combustion:

0.2256 gram substance gave 0.2378 gram H_2O; 0.5723 gram CO_2.

	Calculated.	Found.
C_{10}	69.77	69.18
H_{20}	11.63	11.71
O_2	18.60	...
	100.00	

The ether is a colorless, limpid liquid of a pleasant odor, with a boiling point of 183°.

Dipropyl Acetone.

The oily layer which had separated in the saponification of dipropylethyl acetoacetate was dried with calcium chloride, fractionally distilled and analyzed.

I. 0.1733 gram substance gave 0.2009 gram H_2O; 0.4808 gram CO_2.

II. 0.1544 gram substance gave 0.1797 gram H_2O; 0.4289 gram CO_2.

	Calculated.	Found. I.	Found. II.
C_9	76.06	75.66	75.76
H_{18}	12.67	12.88	12.93
O	11.27	...	...
	100.00		

which results correspond to the formula $\begin{cases} CH_2 \\ CO \\ C(C_3H_7)_2H. \end{cases}$

Dipropyl acetone is a colorless, limpid liquid of a pleasant acetone odor. It boils at 173°–174°, and forms apparently no crystallizable compound with acid sodium sulphite.

Action of Sodium Amalgam upon Dipropylethyl Acetoacetate.

In order to obtain dipropylbetaoxybutyric acid, dipropylethyl acetoacetate was treated with sodium amalgam. A preliminary experiment proved unsuccessful. In repeating it, however, the precaution of neutralizing the free alkali, from time to time, with sulphuric acid was observed. When the reaction was completed, and the whole again neutralized, an oily liquid separated, which was recognized as dipropyl acetone. This being removed, the whole was evaporated to dryness, and repeatedly extracted with alcohol. Out of the alcoholic solution long needles crystallized, which proved to be sodium acetate. The mother-liquor was precipitated with silver nitrate. The precipitate was washed, dried and analyzed.

I. 0.2216 gram silver salt gave 0.3096 gram CO_2, 0.1212 gram H_2O, 0.0944 gram Ag.

II. 0.1215 gram silver salt gave 0.1713 gram CO_2, 0.0677 gram H_2O, 0.0520 gram Ag.

From these results the formula $C_8H_{15}AgO_2$ is deduced.

	Calculated.	Found. I.	Found. II.
C_8	38.25	38.10	38.45
H_{15}	5.98	6.08	6.19
Ag	43.02	42.60	42.80
O_2	12.75	...	...
	100.00		

The composition of this salt shows it to be silver dipropylacetate. In order to establish more fully the fact that dipropylbetaoxybutyric acid had not been formed in the above reaction, the filtrate and washings from the silver salt were precipitated with sodium carbonate, and thus the excess of silver removed. The filtrate now obtained was evaporated and acidified with sulphuric acid, when an oily acid separated. This was removed, converted into the sodium salt, purified with alcohol, and then precipitated with silver nitrate. After washing and drying, the analysis gave the following result:

0.2605 gram gave 0.3577 gram CO_2, 0.1353 gram H_2O, 0.1088 gram Ag.

From which also the formula $C_8H_{15}AgO_2$ may be deduced.

	Calculated.	Found.
C_8	38.25	37.45
H_{15}	5.98	5.76
Ag	43.02	41.77
O_2	12.75	...
	100.00	

The silver salt of dipropylbetaoxybutyric acid $C_{10}H_{19}AgO_3$ has the percentage composition: C, 40.68 per cent.; H, 6.44 per cent.; Ag, 36.61 per cent.; O, 16.27 per cent.

Thus, apparently, none was formed by the action of sodium amalgam upon dipropylethyl acetoacetate, but the latter was, undoubtedly, completely saponified by the action of the free alkali. This reaction is especially interesting, as the diethylethyl acetoacetate can be easily converted into diethylbetaoxybutyric acid without great loss.

Action of Phosphoruspentachloride upon Sodium Diethylbetaoxybutyrate.

It has been shown by Wislicenus[1] that, heating hydracrylic acid and butaoxybutyric acid, acrylic and crotonic acids respectively are formed. Rohrbeck[2] obtained, by treating alphamethyloxybutyric acid, methylcrotonic acid. In a similar manner Schnapp[3] endeavored to obtain alphadiethylisocrotonic acid by the dry distillation of diethyloxybutyric acid thus:

$$\begin{matrix} CH_3 \\ CH.OH \\ C(C_2H_5)_2 \\ CO.OH \end{matrix} - H_2O = \begin{matrix} CH_2{=}CH \\ C(C_2H_5)_2 \\ CO.OH, \end{matrix}$$

but the result was not as anticipated, the only product obtained being diethylacetic acid, accompanied with a strong odor of aldehyde, the molecule having thus split up:

$$\begin{matrix} CH_3 \\ C{<}\begin{matrix} OH \\ H \end{matrix} \\ C(C_2H_5)_2 \\ CO.OH \end{matrix} = \begin{matrix} CH_3 \\ COH \\ \hline CH(C_2H_5)_2 \\ CO.OH. \end{matrix}$$

I endeavored to obtain diethylisocrotonic acid in another manner, viz., by the action of phosphorus pentachloride upon the sodium

[1] Ann. Chem. **166**, 23. Ibid. **149**, 205. Zeitsch. für Chem. 1869, 325.
[2] Ann. Chem, **188**, 229. [3] Ann. Chem. **201**, 62.

salt of diethylbetaoxybutyric acid. The diethylbetachlorbutyric acid formed in the first phase of the reaction, it was anticipated, would lose one molecule of hydrochloric acid, and yield the desired acid, thus —

$$\begin{matrix} CH_3 \\ CHCl \\ C(C_2H_5)_2 \\ CO.OH \end{matrix} - HCl = \begin{matrix} CH_2{=}CH \\ C(C_2H_5)_2 \\ CO.OH. \end{matrix}$$

The sodium diethylbetaoxybutyrate was prepared as described by Schnapp by the action of sodium analgam and water upon diethylethyl acetoacetate, and corresponded in all its properties to those stated by him. In order to effect a more intimate contact of the salt with the phosphorus pentachloride, 18 grams of phosphorus oxychloride were added to 15.8 grams (1 mol.) of the sodium salt, and then 33.2 grams (2 mol.) phosphorus pentachloride were gradually added, and the whole heated on the water-bath with inverted condenser for several hours until the contents of the flask were quite liquid. The product was then poured into water. A dark oily liquid rose to the surface. This was separated, washed with water, and converted into the sodium salt by neutralizing with sodium carbonate, purified by repeatedly extracting with alcohol, and from this the silver salt was prepared. The combustion of this yielded the following results:

I. 0.2178 gram substance gave 0.2561 gram CO_2; 0.1052 gram Ag.

II. 0.2168 gram substance gave 0.2537 gram CO_2; 0.0967 gram H_2O.

III. 0.2201 gram substance gave 0.2563 gram CO_2; 0.1000 gram H_2O; 0.1067 gram Ag.

	Calculated.	Found.		
		I.	II.	III.
C_6	32.28	32.07	31.91	31.76
H_{11}	4.93	...	4.96	5.05
Ag	48.43	48.30	...	48.48
O_2	14.36	...	...	...
	100.00			

These figures show conclusively that the acid formed in the above reaction is diethylacetic acid, which is also confirmed by the fact that its boiling point, 190°–192°, agrees exactly with that of the diethylacetic acid.

According to this then the reaction

$$\begin{matrix} CH_3 \\ CH.OH \\ C(C_2H_5)_2 \\ CO.ONa \end{matrix} + 2PCl_5 = HCl + NaCl + 2POCl_3 + \begin{matrix} CH_3 \\ CHCl \\ C(C_2H_5)_2 \\ CO.Cl \end{matrix}$$

had not taken place, but a splitting up of the molecule into the chloride of diethylacetic acid and a derivative of ethylidene, which latter, however, could not be isolated.

Action of Hydriodic Acid upon Diethyloxybutyric Acid.

The previous experiments having failed to lead to the desired object, the study of the action of diethylbetaoxybutyric acid toward fuming hydriodic acid was then undertaken with the supposition that, if the replacement of the hydroxyl group with hydrogen could in this manner be effected, then triethylacetic acid could be obtained, as expressed by the equation—

$$\begin{matrix} CH_3 \\ CH.OH \\ C(C_2H_5)_2 \\ CO.OH \end{matrix} + 2HI = H_2O + I_2 + \begin{matrix} CH_3 \\ CH_2 \\ C(C_2H_5)_2 \\ CO.OH. \end{matrix}$$

13 grams of well dried sodium diethylbetaoxybutyrate were treated with six times its weight of fuming hydriodic acid in sealed tubes and maintained six hours at a temperature of 120°–125°. On opening the tubes the contents still fumed strongly, and were not under pressure. The dark liquid layer which separated was removed, washed, and the free iodine removed by treating with molecular silver. The oily liquid was dried over sulphuric acid and subjected to fractional distillation. It distilled almost completely over between 190° and 192°.

The combustion gave the following results:

0.2469 gram acid yielded 0.5602 gram CO_2; 0.2333 gram H_2O.

	Calculated.	Found.
C_6	62.07	61.88
H_{12}	10.34	10.50
O^2	27.59	...
	100.00	

The composition and the boiling point show clearly that again diethylacetic acid has been formed, and that a decomposition has taken place analogous to that in the action of phosphorus chloride. Notwithstanding this result, it still seemed not impro-

bable that, by the action of hydriodic acid at ordinary temperature, diethylbetaiodbutyric acid could be formed, which then by treatment with water and sodium amalgam would be converted into triethylacetic acid. In order to test the correctness of this idea 12 grams of the sodium salt were treated with 60 grams of fuming hydriodic acid in a covered beaker glass, and left to stand for several hours. It became quite warm from the reaction, and a dark liquid layer rose to the surface, which after being removed, washed and treated with molecular silver, contained not a trace of chemically combined iodine. The product had the odor of diethylacetic acid, and distilled clearly and completely between 189° and 192°, and was diethylacetic acid, as the combustion showed.

I. 0.2087 gram acid gave 0.4687 gram CO_2; 0.1947 gram H_2O.
II. 0.2000 gram " 0.4500 gram CO_2; 0.1878 gram H_2O.

	Calculated.	Found. I.	Found. II.
C_6	62.07	61.25	61.36
H_{13}	10.34	10.36	10.43
O_2	27.59	...	...
	100.00		

Action of Hydrobromic Acid upon Diethylbetaoxybutyric Acid.

The reaction with hydrobromic acid was undertaken in this case more with a view of establishing the universality of this repeated decomposition of the molecule into aldehyde and diethylacetic acids than in anticipation of a different result. For the experiment 13.3 grams of dry sodium diethylbetaoxybutyrate were treated with 40 grams of fuming hydrobromic acid, and let stand as before for several hours. The dark liquid layer which had separated was removed, washed, dried and fractionally distilled. By far the greatest portion distilled between 190° and 192°, with very slight formation of secondary products. The analysis gave the following result:

0.2342 gram acid gave 0.5294 gram CO_2; 0.2214 gram H_2O.

	Calculated.	Found.
C_6	62.07	61.65
H_{12}	10.34	10.50
O_2	27.59	...
	100.00	

(*To be continued.*)

Contributions from the Sheffield Laboratory of Yale College.

X.—ON ARSENICAL BISMUTH SUBNITRATE.

By R. H. Chittenden and S. W. Lambert.

In 1879, one of us, in conjunction with Prof. S. W. Johnson, made a toxical examination of a human body, in which the finding of arsenic was complicated by the presence of bismuth.[1] The internal organs contained 2.38 grains of arsenious oxide, while the entire muscular and bony tissue contained 2.84 grains of this poison; the distribution being quite regular, as was attested by the results of the individual analyses. The quantity of bismuth found in the stomach and spleen, calculated as $BiNO_4 + H_2O$, was 5.38 grains. The quantity in the liver was a mere trace, wholly unweighable. In the trial which followed, the defense advanced the theory that the arsenic found in the exhumed remains had been absorbed from bismuth, of which the deceased had taken large quantities for medicinal purposes. The frequency with which this theory has been advanced as a plausible defense in similar cases, even when the arsenic has been found in considerable quantities, has led us to make the following experiments, with a view of ascertaining, first, the purity of bismuth subnitrate as regards this poison, and secondly, if arsenic is present, whether the poison is absorbed by the different organs and tissues of the body when repeated doses of the arsenical bismuth are taken.

I. *Examination of Bismuth Subnitrate.*

Dr. Taylor[2] quotes several cases where subnitrate of bismuth, administered in medicinal doses, has produced results directly traceable to arsenic, the presence of which was clearly shown by chemical analysis. Dr. Taylor[3] also mentions that he found arsenic "in comparatively large proportion in samples of the subnitrate, and that only two samples out of five were free from this poison." It has, however, been frequently asserted, on the other hand, that arsenic is but rarely present in bismuth, and then only in the merest trace.

[1] A report of this examination was published in this Journal, **2**, 332.

[2] Treatise on Poisons, 470. [3] *Loc. cit.*

Fourteen distinct samples[1] of bismuth were examined according to the following method: A weighed quantity of the subnitrate was heated in a porcelain caserole with a small quantity of pure sulphuric acid until the nitric acid was completely expelled. The pasty mass of sulphate was then mixed with a small quantity of water and 25 cc. of a dilute sulphuric acid (No. 2), and then fluid and precipitate were introduced into a Marsh apparatus of the form described by Chittenden and Donaldson[2] in the manner there explained. The greater part of the bismuth was washed into the apparatus by the use of acids Nos. 3 and 4,[3] frothing being prevented, when necessary, by the use of a few drops of sweet oil. When the evolution of hydrogen had wholly ceased, the mirror of metallic arsenic was weighed, the arsenic being afterwards removed from the weighed portion of the tube by volatilization.

Preliminary experiments were made to ascertain whether the presence of bismuth has any influence on the liberation of arsenic as arsenuretted hydrogen. Definite amounts of arsenious oxide were added to arsenic-free bismuth, and the mixtures, after heating with sulphuric acid, were introduced into the Marsh apparatus, with the following results:

Quantity of arsenic used.	Wt. of met. arsenic found when mixed with bismuth.	Wt. of met. arsenic found when introduced alone.	Theoretical wt. of met. arsenic.
.004 gram As_2O_3.	.00290	.00300	.00303
.004 " "	.00280	.00290	.00303
.003 " "	.00210	.00225	.00227

Where the amount of bismuth taken was over five grams, there appeared to be occasionally a slight loss of arsenic, owing presumably to the mechanical hindrance caused by the presence of such a large amount of insoluble matter.

The samples of bismuth were analyzed with the following results:

[1] Obtained from various places in New York, Philadelphia and New Haven.
[2] This Journal, 2, 235. [3] *Loc. cit.*

	Subnitrate taken.	Wt. of As found.	Quantity of As in 100 grams bism'h.	Quantity of As_2O_3 in 100 grams bism'h.
No. 1	4.5111 grams	.00040 gram	.00886 gram	.01169 gram
" 2	4.5141 "	.00035 "	.00775 "	.01023 "
" 3	4.5012 "	trace.		
" 4	4.5017 "	trace.		
" 5	4.5016 "	.00070 "	.01550 "	.02040 "
" 6	4.5010 "	.00030 "	.00660 "	.00870 "
" 7	4.5048 "	.0002 "	.00440 "	.00588 "
" 8	4.5123 "	.00015 "	.00330 "	.00435 "
" 9	4.5273 "	.00040 "	.00883 "	.01148 "
" 10	6.4208 "	.00080 "	.01234 "	.01630 "
" 11	5.1000 "	.00038 "	.00742 "	.00980 "
" 12	4.2128 "	.00020 "	.00474 "	.00626 "
" 13	2.5650[1] "	.00156 "	.05847 "	.07719 "
" 14	10.054 "	.0		
	Average of the fourteen determinations		.01302	"

The weighings were made on an exceedingly delicate balance, and several of the analyses were duplicated as follows:

No. 11
1. 5.100 grams substance gave .00038 gram As=.0098 per cent. As_2O_3.
2. 4.020 grams substance gave .0003 gram As=.0098 per cent. As_2O_3.

No. 9
1. 4.5273 grams substance gave .0004 gram As=.01148 per cent. As_2O_3.
2. 10.000 grams substance gave .0008 gram As=.01056 per cent. As_2O_3.
3. 4.500 grams substance gave .0005 gram As=.01475 per cent. As_2O_3.

No. 2
1. 4.5141 grams substance gave .00035 gram As=.01023 per cent. As_2O_3.
2. 4.5022 grams substance gave .0003 gram As=.00879 per cent. As_2O_3.

These results show how far reliance is to be placed upon the weighing of such minute quantities, and indicate the differences to be expected in duplicate analyses made in this manner. In the three analyses of sample No. 9, it is to be noticed that the first and second results show a difference of only .00092 per cent. of As_2O_3, while in the second and third results, where there is a greater

[1] Basic carbonate of bismuth.

variation, the difference amounts to but .00419 per cent. As_2O_3; the average difference being much less.

It was next to be ascertained whether the metallic mirrors obtained in this manner were really arsenic, since from the usual methods of preparation of bismuth subnitrate, antimony might be present. Several of the mirrors were treated with pure and dry hydrogen sulphide gas, when, with the aid of a gentle heat, the dark metallic mirror changed to a *bright yellow* color. Again, several mirrors were treated separately with pure nitric acid. The solutions on evaporation left a small white residue, readily soluble in a drop of water. A drop of concentrated silver nitrate solution added to this residue produced a heavy brick-dust red precipitate of silver *arsenate*, readily soluble in ammonia, thus showing without doubt the presence of arsenic.

From an examination of the results obtained, it is seen that only one sample out of the fourteen analyzed is absolutely free from arsenic, while the average content of poison in the samples examined is .013 per cent., or 13 milligrams of arsenious oxide in 100 grams of bismuth. This amount is equivalent to two-tenths of a grain of arsenious oxide. In sample No. 13 the amount is not so insignificant. Here 100 grams of the basic carbonate of bismuth contain 77 milligrams of arsenious oxide, or 1.2 grains, which constitutes half a fatal dose of this poison. The subnitrate of bismuth in particular is a medicine very extensively used, and though it may not contain arsenic in sufficient quantity to be in itself productive of harm, still the presence of such a poison in so common a medicine is greatly to be deplored, from the unjust conclusions and serious mistakes it is liable to cause.

II. *Absorption of Arsenic from Bismuth Subnitrate.*

Arsenic is not strictly an accumulative poison. It accumulates for a time in certain of the organs and tissues of the body, but elimination soon commences, and if all the excretory functions are in normal condition, it is very questionable whether there can be any great retention or accumulation of the poison by the various organs of the body when very small quantities are taken at periods somewhat remote from each other. It is a very important question whether the elimination of arsenic in the living body goes on with the same degree of rapidity as its absorption. All the facts at present, how-

ever, point to a rapid and eventually a complete elimination of the poison; still there is no evidence to show that even such small quantities of arsenic as are present in these samples of bismuth may not be absorbed and give rise to an appreciable accumulation of this poison in the various organs of the body. It has therefore seemed desirable to ascertain exactly to how great an extent arsenic is absorbed and retained when arsenical bismuth is taken. A large and healthy dog was therefore selected, and a given quantity of bismuth subnitrate was administered to him three times daily with his food, in gradually increasing doses. The feeding of bismuth was commenced on the morning of March 12th, and continued without interruption until April 19th, the last dose being given at night. On April 20th, 24 hours after the last dose of bismuth was given, the dog was killed, and the various organs and a portion of the muscular tissue were preserved for analysis.

The bismuth used was sample No. 9, which contained, according to the average of the three analyses made, .01226 per cent. of arsenious oxide. The bismuth was given at first in doses of .0648 gram. On the third day .1296 gram was given, on the sixth .5184 gram three times daily. The dose was then rapidly increased, until on the 28th of March 6.48 grams were given three times a day, which dose was continued until April 19th, the end of the experiment. During the entire period of five weeks 539 grams of bismuth subnitrate were given, which quantity must have contained .06608 gram, or a little more than one grain of arsenious oxide. The amount of arsenic taken per day in the bismuth for the last three weeks was 2.38 milligrams.

The dog was apparently unaffected by the bismuth. A post mortem examination of the stomach showed the mucous membrane slightly congested in a few places. The various organs of the body were subjected individually to analysis for arsenic, and in several cases for bismuth also. The organs were examined for arsenic by the method described by Chittenden and Donaldson,[1] while for bismuth, portions of tissue were oxidized in the usual manner by hydrochloric acid and potassium chlorate according to the method of Fresenius and Babo. The results of the analyses were as follows:

[1] This Journal, 2, 235.

	Weight of dry tissue.	Amount of metallic arsenic found.	
Stomach,	250 grams	.00036 gram.	
Large Intestines,	85 "	.0006 "	
Small Intestines,	300 "	.0002 "	
Liver,	415 "	In these organs, distinct mirrors were obtained which, though unweighable, were easily arranged in the accompanying order, as regards amount.	
Spleen,	23 "		
Brain,	45 "		
Blood (not dried)	552 "		
Kidneys,	54 "	In these organs, exceedingly minute stains were obtained, too small to be identified other than as the merest brown spots.[1]	
Heart,	81 "		
Lungs,	114 "		
Muscle (thigh)	216 "		

In the stomach and intestines bismuth was found in considerable quantities. In the liver and blood, on the other hand, only a very small trace was found, thus showing the difficulty with which bismuth is absorbed. From the above results we can conclude, then, that the greater part of the arsenic taken in the bismuth was not absorbed. For a period of three weeks 2.38 milligrams of arsenious oxide were taken each day. This amount if absorbed would have given a much larger content of arsenic for the various organs of the body than was found. Even supposing the rate of elimination to have been equal in this case to the rate of absorption, still then we must have found an appreciable amount of arsenic in the kidneys, since it has been clearly proven that the greater part of absorbed arsenic is eliminated by these organs. Again, the amount of arsenic found in the alimentary canal, particularly in the large intestines, was only one-half the amount contained in the last three doses of bismuth taken, a portion of which remained in the alimentary canal at the time of death. This then was not absorbed arsenic, but simply the amount contained in the bismuth still remaining in the alimentary canal. The amount found in the liver, brain and blood is, however, evidence of slight absorption.

The non-absorption of the arsenic is probably dependent upon the form in which it exists in the bismuth. If present in the form of arsenious oxide it would be readily dissolved by water. According to Taylor,[2] hot water cooling from 100° C. on arsenious oxide in powder, dissolves about the 400th part of its weight, which is approximately in the proportion of 77 milligrams of arsenious

[1] All the chemicals employed in the analyses were absolutely free from arsenic, giving no deposit whatever in the Marsh apparatus.

[2] Treatise on Poisons, 287.

oxide to 30 cc. of water. Five grams of bismuth subnitrate, sample No. 1, were treated with about 350 cc. of boiling water, which was allowed to cool on the powder with occasional agitation. When nearly cold the fluid was filtered off and the residual bismuth washed with about 250 cc. of boiling water. Filtrate and washings were then evaporated nearly to dryness on the water-bath, and the residue, dissolved in sulphuric acid No. 2, was introduced into the Marsh apparatus. Not even a trace of a mirror was obtained. Considerable bismuth had been dissolved, but no arsenic, thus apparently showing that the arsenic exists in the bismuth salt in some form other than arsenious oxide. The non-absorption of the arsenic depends then on its insolubility. The arsenic is however completely dissolved by dilute sulphuric acid; thus 10 grams of bismuth subnitrate, sample No. 9, were dissolved in a moderate quantity of dilute sulphuric acid, from which the bismuth separated again almost immediately as crystalline bismuth sulphate. By washing this precipitate with an abundance of water the arsenic was wholly removed from the bismuth, and by introducing the evaporated filtrate and washings into the Marsh apparatus the entire amount of arsenic was obtained. We can then conclude from our experiments that while medicinal bismuth subnitrate contains a weighable quantity of arsenic, the poison is not present in the samples which we have experimented with, in a form capable of being readily absorbed into the system. This fact however does not diminish the need for a preparation of bismuth entirely free from arsenic.

RESEARCHES ON THE COMPLEX INORGANIC ACIDS.

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(Continued from p. 332.)

Five to One Series.—Salts of this series were discovered at an early period in the history of the subject by Zenker.[1] The ammonium salt was analyzed by Zenker[2] and Werncke,[3] and recently

[1] Journal für prakt. Chemie, **58**, 256. [2] *Loc. cit.* [3] Zeitschrift für analyt. Chemie, **14**, 12.

by Rammelsberg.[1] Debray obtained the same salt, but has published no analyses. Rammelsberg also obtained the corresponding potassium salt, as well as an acid salt of the same series. The alkaline salts are colorless, and separate in well-defined crystals, which are usually easily soluble in water. The acid of the series, as Debray has stated, cannot be obtained by the decomposition of its salts, being resolved by acids into free phosphoric acid and salts of the 24-atom series. The decomposition may probably be expressed by the equation

$$24(5MoO_3.P_2O_5.3H_2O) = 5(24MoO_3.P_2O_5.3H_2O) + 19(P_2O_5.3H_2O).$$

All the neutral salts are tribasic (old style), or more correctly hexatomic, but well-defined acid salts exist in which the ratio of the molybdic oxide to the fixed base is as 10 : 5. Such salts have been obtained by Rammelsberg and by myself. The salts of the higher series are decomposed by alkalies, as stated by Debray, salts of the 5-atom series and alkaline molybdates being formed. Conversely, when a mineral acid is added to a solution of an alkaline salt of the 5-atom series, a salt of a higher series is formed, frequently as a yellow crystalline precipitate. The neutral salts of this series hitherto described have respectively the formulas

$$5MoO_3.P_2O_5.3K_2O + 7aq.$$
$$5MoO_3.P_2O_5.3(NH_4)_2O + 7aq.$$
$$5MoO_3.P_2O_5.3Na_2O + 14aq.$$
$$5MoO_3.P_2O_5.3Ag_2O + 7aq.$$

5 : 3 *Phospho-molybdate of Ammonium.*—This beautiful salt appears, as already stated, to have been first obtained by Zenker. It is readily obtained by dissolving together five molecules of ammonic molybdate and two of ammonic phosphate, and evaporating the solution, when beautiful prismatic crystals, with a glassy lustre, separate. These may easily be purified by recrystallization. The salt is readily soluble in hot, less easily in cold water. The solution has an acid reaction. Zenker's analyses, as well as those of Werncke, agree closely with the formula

$$5MoO_3.P_2O_5.3(NH_4)_2O + 7aq,$$

[1] *Loc. cit.*

in which formula the phospho-molybdic acid is regarded as tribasic. Debray gives the same formula, without details of analysis, and Rammelsberg has very recently again analyzed the salt, confirming the results of Zenker. The salt in question is particularly interesting, first, because the number of atoms of molybdic oxide is *uneven;* and secondly, because the basicity of the acid appears to be 3, and not 6, even when the salt has separated from neutral solutions.

Jörgensen[1] has described two well-defined crystalline salts belonging to this series, and having according to his notation respectively the formulas

$$Co_2(NH_3)_{10}Cl_2.(5MoO_3.2PO_4H)$$

and

$$Co_2(NH_3)_{10}Cl_2.(5MoO_3.2PO_4NH_4).$$

I should write these

$$5MoO_3.P_2O_5.Co_2(NH_3)_{10}Cl_2O_2.H_2O$$

and

$$5MoO_3.P_2O_5.Co_2(NH_3)_{10}Cl_2O_2(NH_4)_2O.$$

It will readily be seen that both salts correspond to the acid represented by the formula

$$5MoO_3.P_2O_5.H_2O.$$

Acid 10 : 5 *Ammonium Salt.*— When ammonic phosphate is dissolved in boiling water, and molybdic oxide is added in small portions at a time, the oxide readily dissolves, but a greater or less quantity of a white insoluble crystalline salt is formed. The filtrate deposits on evaporation large colorless crystals, which appear to be either trimetric or monoclinic. Of these crystals,—

1.1126 gram lost on ignition with WO_4Na_2 0.2076 gram = 18.66 per cent. NH_3 and H_2O.

1.2962 gram lost on ignition with WO_4Na_2 0.2425 gram = 18.71 per cent. NH_3 and H_2O.

1.2165 gram lost on ignition with WO_4Na_2 0.2247 gram = 18.47 per cent. NH_3 and H_2O.

0.9263 gram gave 0.1912 gram $P_2O_7Mg_2$ = 13.20 per cent. P_2O_5.

1.0540 gram gave 0.2196 gram $P_2O_7Mg_2$ = 13.32 per cent. P_2O_5.

[1] Journal für prakt. Chemie, [2] **18**, 209.

1.1824 gram gave 0.3018 gram NH_4Cl = 12.41 per cent. $(NH_4)_2O$.

1.0183 gram gave 0.2563 gram NH_4Cl = 12.23 per cent. $(NH_4)_2O$.

1.6430 gram gave 0.4168 gram NH_4Cl = 12.32 per cent. $(NH_4)_2O$.

The analyses lead to the formula

$$10MoO_3.2P_2O_5.5(NH_4)_2O.H_2O+6aq,$$

or

$$5MoO_3.P_2O_5.3(NH_4)_2O+5MoO_3.P_2O_5.2(NH_4)_2O.H_2O+6aq,$$

which requires:

		Calc'd.	Mean.			
$10MoO_3$	1440	68.24	68.13	...	...	...
$2P_2O_5$	284	13.46	13.26	13.20	13.32	...
$5(NH_4)_2O$	260	12.32	12.32	12.41	12.23	12.32
$7H_2O$	126	5.98	6.29	6.15	6.34	6.39
	2110	100.00				

The phosphoric oxide was determined by double precipitation only, without subsequent treatment with ammonic sulphide. The percentage is a little lower than that required by the formula, which is unusual; but the general agreement of the analyses with the formula is satisfactory. Rammelsberg has described an acid potassium salt with the formula

$$10MoO_3.P_2O_5.5K_2O.H_2O+19aq.$$

It is therefore at least probable that we shall find another ammonia salt with 20 atoms of water, and another potassium salt with 7 atoms. Zenker has described another potassic salt to which he gives the formula,—as I should write it,—

$$9MoO_3.P_2O_5.4K_2O.2H_2O+18aq;$$

but the results of his analyses differ very widely from the percentages required by the formula, and on repeating his process I obtained only the 10:5 atom salt of Rammelsberg. The formula given above for this salt requires 11.11 per cent. P_2O_5. I found 11.22 per cent.

Rammelsberg[1] has also described a white insoluble potassium salt to which he gives the formula $15MoO_3.P_2O_5.5K_2O$, but without any statement of his analyses.

[1] *Loc. cit.*

ARSENIO-MOLYBDATES.

Compounds of arsenic and molybdic oxides have been described by Seyberth[1] and by Debray.[2] Seyberth obtained an acid with the formula,—as I should write it,—

$$7MoO_3.As_2O_5.3H_2O+11aq,$$

and the three corresponding salts:

$$7MoO_3.As_2O_5.(NH_4)_2O.2H_2O+4H_2O$$
$$7MoO_3.As_2O_5.3BaO$$
$$7MoO_3.As_2O_5.3Ag_2O.$$

Debray obtained the acids and one or two salts of two different series, which may be represented respectively by the formulas:

$$20MoO_3.As_2O_5.3H_2O+24aq$$
$$20MoO_3.As_2O_5.3K_2O$$
$$20MoO_3.As_2O_5.3(NH_4)_2O$$
$$6MoO_3.As_2O_5.3H_2O+13aq$$
$$6MoO_3.As_2O_5.4(NH_4)_2O+aq$$
$$6MoO_3.As_2O_5.(NH_4)_2O+4aq$$
$$6MoO_3.As_2O_5.NaO_2+12aq.$$

Debray considers the formula of the 20-atom ammonium salt as probable only, and regards the water determination in the corresponding acid as not quite certain. Neither Seyberth nor Debray has described the analytical methods employed, or given the details of the analyses.

I have found it most advantageous to separate arsenic from molybdic oxide by precipitating with magnesia mixture, redissolving the ammonio-magnesic arsenate, and precipitating a second time with ammonia after adding a little magnesia mixture. The ammonio-magnesic arsenate may be digested with ammonic sulphide without decomposition; but after the second precipitation it does not retain molybdic oxide, and the subsequent treatment is therefore unnecessary. To determine the sum of the molybdic and arsenic oxides I precipitate the two together with mercurous nitrate and mercuric oxide, in the manner already described for the estimation of molybdic and phosphoric oxides, filter upon paper, and after drying roll up the filter and its contents and ignite cautiously

[1] Berichte der deutsch. chem. Gesellschaft, 1874, 391. [2] Comptes Rendus, **78**, 1408.

in a porcelain crucible. By slow and careful heating the filter may be completely burned without loss of molybdic or arsenic oxides, this result being attained by the oxygen of the mercurous and mercuric oxides present. A weighed quantity of sodic tungstate is then to be added in fine powder, the mass well mixed in the crucible, and then cautiously heated until mercury is completely expelled, and after cooling a white fused mass remains. A second or even a third heating is necessary to insure a perfectly constant weight. The difference between the percentage of arsenic oxide, As_2O_5, and the sum of the percentages of the arsenic and molybdic oxides, gives the percentages of molybdic oxide with a very fair degree of approximation. In these salts the water must always be determined by ignition with sodic tungstate or some similar compound, since both arsenic and molybdic oxides are volatile.

Sixteen to one Series.—When solutions of ammonic arsenate and acid molybdate (7 : 3 salt) are mixed, a beautiful white crystalline precipitate is thrown down, which is very insoluble in cold water, but dissolves slightly in boiling water, giving, however, a turbid solution. The salt is readily soluble in ammonia water. The portion analyzed was well washed on a filter with cold water and dried on woollen paper. In this salt,—

1.1322 gram lost on ignition with WO_4Na_2 0.1636 gram NH_3 and H_2O = 14.45 per cent.

1.3389 gram gave 0.2481 gram NH_4Cl = 9.00 per cent. $(NH_4)_2O$.

1.4276 gram gave 0.1478 gram $As_2O_7Mg_2$ = 7.68 per cent. As_2O_5.

The analyses lead to the formula

$$16MoO_3.As_2O_5.5(NH_4)_2O.H_2O+8aq.$$

which requires :

		Calc'd.			
$16MoO_3$	2304	77.94	85.72	77.97	85.65
As_2O_5	230	7.78		7.68	
$5(NH_4)_2O$	260	8.79	14.28	9.00	14.45
$9H_2O$	162	5.49		5.45	
	2956				

The salt may have lost a little ammonia in drying. When potassic arsenate and acid molybdate are mixed, a similar salt is formed. A solution of arsenic acid gives at once in solutions of

acid ammonic or potassic molybdate a beautiful white crystalline precipitate, insoluble in cold water, but soluble in a large quantity of boiling water, forming cloudy solutions which pass freely through a filter. These may serve as starting-points for new investigations. The arsenio-molybdate above described is not perceptibly altered by long boiling with nitric acid, but the existence of higher compounds containing 22 or 24 molecules of molybdic to one of arsenic oxide appears at least extremely probable.

The phospho-molybdates and arsenio-molybdates now known with some degree of certainty are as follows:

$24MoO_3.P_2O_5.6H_2O+47aq$	$Mo_{24}P_2O_{71}(HO)_{12}+47aq$
$24MoO_3.P_2O_5.6H_2O+43aq$	$Mo_{24}P_2O_{71}(HO)_{12}+43aq$
$24MoO_3.P_2O_5.6H_2O+24aq$	$Mo_{24}P_2O_{71}(HO)_{12}+24aq$
$24MoO_3.P_2O_5.2K_2O.4H_2O$	$Mo_{24}P_2O_{71}(KO)_4(HO)_8$
$24MoO_3.P_2O_5.CcO.5H_2O+18aq$	$Mo_{24}P_2O_{71}(CcO_2)(HO)_{10}+18aq$
$48MoO_3.2P_2O_5.5(NH_4)_2O.H_2O+16aq$	$Mo_{48}P_4O_{148}(NH_4O)_{10}(HO)_2+16aq$
$22MoO_3.P_2O_5.3(NH_4)_2O.3H_2O+9aq$	$Mo_{22}P_2O_{65}(NH_4O)_6(HO)_6+9aq$
$22MoO_3.P_2O_5.3(NH_4)_2O.3H_2O+6aq$	$Mo_{22}P_2O_{65}(NH_4O)_6(HO)_6+6aq$
$22MoO_3.P_2O_5.3(NH_4)_2O$	$Mo_{22}P_2O_{65}(NH_4O)_6$
$22MoO_3.P_2O_5.3K_2O.3H_2O+9aq$	$Mo_{22}P_2O_{65}(KO)_6(HO)_6+9aq$
$22MoO_3.P_2O_5.7Ag_2O+14aq$	$Mo_{22}P_2O_{64}(AgO)_{14}+14aq$
$44MoO_3.2P_2O_5.5K_2O.H_2O+21aq$	$Mo_{44}P_4O_{130}(KO)_{10}(HO)_2+21aq$
$60MoO_3.3P_2O_5.8(NH_4)_2O.H_2O+11aq$	$Mo_{60}P_6O_{186}(NH_4O)_{16}(HO)_2+11aq$
$18MoO_3.P_2O_5.Na_2O.5H_2O+maq$	$Mo_{18}P_2O_{62}(NaO)_3(HO)_{10}+maq$
$18MoO_3.P_2O_5.2Na_2O.4H_2O+naq$	$Mo_{18}P_2O_{54}(NaO)_4(HO)_8+naq$
$16MoO_3.P_2O_5.3(NH_4)_2O.3H_2O+11aq$	$Mo_{16}P_2O_{47}(NH_4O)_6(HO)_6+11aq$
$5MoO_3.P_2O_5.3Na_2O.3H_2O+11aq$	$Mo_5P_2O_{14}(NaO)_6(HO_6)+11aq$
$5MoO_3.P_2O_5.3(NH_4)_2O.3H_2O+4aq$	$Mo_5P_2O_{14}(NH_4O)_6(HO)_6+4aq$
$5MoO_3.P_2O_5.3K_2O.3H_2O+4aq$	$Mo_5P_2O_{14}(KO)_6(HO)_6+4aq$
$5MoO_3.P_2O_5.3Ag_2O.3H_2O+4aq$	$Mo_5P_2O_{14}(AgO)_6(HO)_6+4aq$
$10MoO_3.2P_2O_5.K_2O.H_2O+19aq$	$Mo_{10}P_4O_{34}(KO)_{10}(HO)_2+19aq$
$10MoO_3.2P_2O_5.5(NH_4)_2O.H_2O+6aq$	$Mo_{10}P_4O_{34}(NH_4O)_{10}(HO)_2+6aq$
$20MoO_3.As_2O_5.6H_2O+21aq$	$Mo_{20}As_2O_{59}(HO)_{12}+21aq$
$20MoO_3.As_2O_5.3K_2O$	$Mo_{20}As_2O_{62}(KO)_6$
$20MoO_3.As_2O_5.3(NH_4)_2O$	$Mo_{20}As_2O_{62}(NH_4O)_6$
$16MoO_3.As_2O_5.5(NH_4)_2O.H_2O+8aq$	$Mo_{16}As_2O_{47}(NH_4O)_{10}(HO)_2+8aq$

$7MoO_3.As_2O_5.6H_2O+aq$	$Mo_7As_2O_{20}(HO)_{12}+8aq$
$7MoO_3.As_2O_5.(NH_4)_2O.5H_2O$	$Mo_7As_2O_{20}(NH_4O)_2(HO)_{10}$
$7MoO_3.As_2O_5.3BaO$	$Mo_7As_2O_{23}(BaO_2)_3$
$7MoO_3.As_2O_5.3Ag_2O$	$Mo_7As_2O_{23}(AgO)_6$
$6MoO_3.As_2O_5.6H_2O+10aq$	$Mo_6As_2O_{17}(HO)_{12}+10aq$
$6MoO_3.As_2O_5\ 4(NH_4)_2O+aq$	$Mo_6As_2O_{19}(NH_4O)_8$
$6MoO_3.As_2O_5.(NH_4)_2O.2H_2O+aq$	$Mo_6As_2O_{20}(NH_4O)_2(HO)_4+2aq$
$6MoO_3.As_2O_5.Na_2O.5H_2O+7aq$	$Mo_6As_2O_{17}(NaO)_2(HO)_{10}+7aq$

For the convenience of comparison with the corresponding compounds of tungsten, I have in writing these formulas as far as possible assumed that all the phospho-molybdic and arsenio-molybdic acids contain 12 atoms of hydroxyl, or, in the language appropriate to the old notation, are six-basic. With the material before us, we are now prepared to discuss the question of the basicity of the phospho-tungstates and phospho-molybdates as well as of the corresponding arsenic compounds.

The general results to which the study of the phospho-molybdates and arsenio-molybdates has led are as follows:

1. The phospho-molybdates form a series of which the lowest term contains five atoms of molybdic to one of phosphoric oxide, and the highest twenty-four atoms of the former to one of the latter.

2. As in the case of the phospho-tungstates, the greater number of the molybdenum compounds contain an even number of atoms of tungstic acid. The homologizing term is therefore $2MoO_3$ for these cases.

3. By far the greater number of phospho-molybdates contain *three* atoms of fixed base (old style), or, in more modern language, may be considered as derived from acids containing *six* atoms of hydroxyl. Anhydrous compounds of this type occur, and are not always simply residues obtained by heating salts which may be considered as acid, as containing, for example, $3R_2O.3R_2O$. It seems therefore necessary to admit the existence of acids of the general type

$$nMoO_3.P_2O_5.3H_2O,$$

which may, however, stand in the relation of pyro-acids to other acids of the type

$$nMoO_3.P_2O_5.6H_2O.$$

4. On the other hand, while no single phospho-molybdate containing more than three atoms of fixed base for one of phosphoric

oxide has been obtained in a state of indubitable purity, it is probable that there is at least one salt with *six* or more atoms of fixed base. I refer to the silver salt which I have expressed by the formula

$$22MoO_3.P_2O_5.7Ag_2O+14aq.$$

5. Setting aside the evidence derived from the analogy of the phospho-molybdates and phospho-tungstates, there is at present no sufficient proof of the existence of a series of phospho-molybdates or arsenio-molybdates containing more than *three* atoms of fixed base. Such purely negative evidence must not be too highly regarded.

6. As in the case of the phospho-tungstates, there exists a class of phospho-molybdates in which the ratio of the number of atoms of base to that of the number of atoms of phosphoric oxide is as 5 : 2, the number of atoms of molybdic oxide being even.

Since the publication of my work on the phospho-tungstates and arsenio-tungstates, a paper by Sprenger[1] on the phospho-tungstates has appeared. Sprenger has examined, with a single exception, only the compounds of the 24 : 1 series, and has added a number of new salts, which, so far as regards their constitution, fully confirm my own results. The compounds described, belonging to the 24-atom series, are the following:

$$24WO_3.P_2O_5.3H_2O+58aq$$
$$24WO_3.P_2O_5.3BaO+58aq$$
$$24WO_3.P_2O_5.2BaO.H_2O+58aq$$
$$24WO_3.P_2O_5.BaO.2H_2O+58aq$$
$$24WO_3.P_2O_5.3Cu_2O+58aq$$
$$24WO_3.P_2O_5.3Ag_2O+58aq$$
$$24WO_3.P_2O_5.2Ag_2O.H_2O+58aq.$$

Sprenger's formula for the octahedral acid agrees with that which I had given if we consider the acid as tribasic. The other salts which he has described are new, and form a valuable addition to our knowledge of this class of compounds. It is well worthy of notice, that in all of his salts, the acid included, the number of atoms of water is the same. The acid with 58 atoms of water of crystallization forms, therefore, a complete and stable molecular structure in which 2, 4, or 6 atoms of hydrogen are replaceable. I do not recall any other series in which this constancy of crystalline water occurs,

[1] Journal für prakt. Chemie, **22**, 418.

at least to the same extent. Sprenger has also obtained a salt of the 22-atom series which is of much interest. This is the barium salt,

$$22WO_3.P_2O_5.7BaO+59\tfrac{1}{2}aq,$$

and its special interest depends upon the fact, first, that the ratio of the tungstic to the phosphoric oxide is as 22 : 1, and, secondly, that the salt contains *seven* atoms of fixed base, or, in other words, must be considered as derived from an acid containing at least *fourteen* atoms of hydroxyl. Sprenger asserts that he has obtained the corresponding acid, and it is to be hoped that he will pursue the subject farther. This barium compound furnishes additional evidence of the independent existence of a series in which the ratio is 22 : 1, and in addition it renders more probable the formula which I have given for Debray's silver salt,

$$22MoO_3.P_2O_5.7Ag_2+14aq.$$

From these two tolerably well-established cases it would appear that we are not justified in holding that the phospho-tungstates, phospho-molybdates, and corresponding arsenic compounds, have a basicity of which the higher limit is six. I may here mention that I shall hereafter describe a vanadio-molybdate of ammonium, the analyses of which agree well with the formula

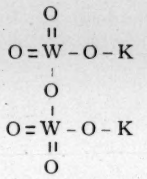
$$18MoO_3.V_2O_5.8(NH_4)_2O+15aq.$$

The risk of drawing hasty conclusions from purely negative evidence is particularly great in discussing the degree of basicity of this whole class of compounds, but I shall endeavor to show that it is possible to devise structural formulas which will embrace and explain all degrees of basicity which appear to be possible under the general conditions of the problem.

We may, as in the case of the alkaline tungstates already discussed, assume that both tungsten and molybdenum are hexatomic, and, as in that case, we may start from the commonly received formula for potassic dichromate,

$$\begin{array}{c} CrO_2-O-K \\ | \\ O \\ | \\ CrO_2-O-K \end{array}$$

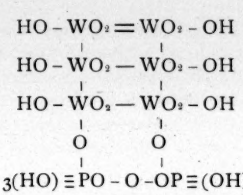
which may be equally well applied to hexatomic tungsten,



If we further suppose that the separate terms of the structural formulas are symmetrically arranged, and take a 6 : 1 phosphotungstate

$$6WO_3.P_2O_5.6H_2O \quad \text{or} \quad 6WO_2.P_2O_5.(HO)_{12}$$

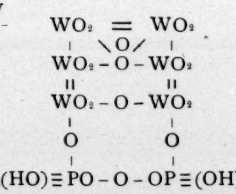
as an illustration, we may, with at least a certain degree of probability, express the structure as follows:



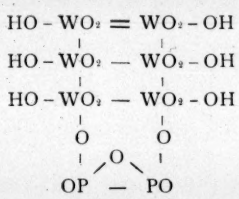
This formula explains the basicity of the acid satisfactorily. It also shows that, as six atoms of hydroxyl are united with phosphorus, and six with tungstic oxide, there should be theoretically a limiting case corresponding to an acid containing six atoms of hydroxyl, and represented by the formula

$$6WO_3.P_2O_5.3H_2O \quad \text{or} \quad 6WO_2.O_2.P_2O_5.(HO)_6$$

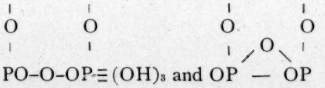
and structurally by



According to this view six atoms of hydroxyl are always associated with phosphorus, or, as the case may be, with arsenic. I consider this view of the subject by far the more probable. At the same time, however, it is also possible that we may have the structural formula,



in which all the atoms of hydroxyl are associated directly with tungsten, and in the present state of our knowledge we can only decide the question upon general grounds of probability, so that our conclusions are at best uncertain. Finally, both formulas being at least possible, it may be that there are two isomeric modifications of each series of acids represented respectively by the formulas above given. There is no present evidence of the existence of such isomeric modifications in the case of phospho-tungstates, phospho-molybdates, or the corresponding arsenic series; but Marignac has shown that there are two isomeric series of silico-tungstates, which he calls respectively silico-tungstates and tungsto-silicates, and it may be that the difference between these depends upon differences in the mode of combination, precisely similar to those which I have pointed out above. I shall return to this subject in the general discussion of my results. With respect to the two linking terms,

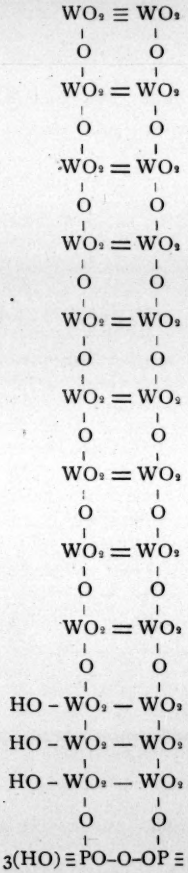


no assumption is made which is not in perfect accordance with commonly accepted views of the subject.

We may now consider the most general case, that, namely, in which there are twenty-four atoms of tungstic or molybdic to one of phosphoric or arsenic oxide. We have for an acid of this type

$$24WO_3.P_2O_5.6H_2O \quad \text{or} \quad 24WO_2.O_{18}.P_2O_5.(HO)_{12}$$

and in accordance with the principles above laid down the structural formula may be written:



The case of an acid containing for twenty-four atoms of tungstic oxide six atoms of hydroxyl may easily be deduced from the above, upon the principle explained in the first example cited. Without again writing the cumbrous formula, it may easily be seen that the cases of acids containing more than twelve atoms of hydroxyl, if such really exist, are embraced in the above given structural formula; and that in such cases there will be two variations in the mode of combination of the hydroxyl, similar to the two which occur when there are six or twelve atoms of hydroxyl. The structural formula given would explain simply and naturally the *tribasic* character of all known phospho-molybdates and phospho-tungstates containing twenty-four atoms of metallic oxide, since in these all the hydroxyl may be united with phosphorus exclusively, or with tungsten exclusively. It only remains to consider the case of the compounds having for one atom of phosphoric or arsenic oxide an *uneven* number of atoms of metallic oxide, as, for instance, the 5 : 1 and 7 : 1 series. In these cases also there exists, as has been shown, a second and derived series, of which the successive terms are to be regarded as formed from those of the first series by doubling the molecular weight and dropping an atom of fixed base. Thus, we have

$5MoO_3.P_2O_5.3H_2O$ and	$10MoO_3.2P_2O_5.5K_2O.H_2O+19aq$
$7MoO_3.As_2O_5.3H_2O$	$14WO_3.2P_2O_5.5Na_2O.H_2O+42aq$
$22MoO_3.P_2O_5.3H_2O$	$44MoO_3.2P_2O_5.5K_2O.H_2O+21aq$
$24MoO_3.P_2O_5.3H_2O$	$48MoO_3.2P_2O_5.5(NH_4)_2O.H_2O+16aq$

All these salts appear to have an acid reaction. They may all be regarded as acid six-basic salts, and it is easy to see that the two series may be reduced to one by doubling the formulas of all the terms on the left, so that we shall have a single series, of which the successive terms are

$10MoO_3.2P_2O_5.6H_2O$
$12MoO_3.2As_2O_5.6H_2O$
$14WO_3.2P_2O_5.6H_2O$
. . . . . .
$48MoO_3.2P_2O_5.6H_2O$

This view in nowise excludes acids or salts of a higher degree of basicity. It has the advantage of bringing all the compounds together, and of being more completely in accordance with what

we know of the constitution of salts belonging to simpler types. The structural formulas which I have given—provisionally, of course—may easily be modified to suit this view, and will all be symmetrical and suggestive of various possible isomerisms.

The study of other complex inorganic acids will, doubtless, throw further light upon the subject, and to it I shall continue to devote my leisure. It already begins to appear that inorganic compounds may possess an unexpected degree of complexity, and that very wide fields of research in inorganic chemistry are still open.

(*To be continued.*)

THE QUANTITATIVE SEPARATION OF ROSIN FROM FATS.

By Thomas S. Gladding.

The need of an accurate process for the separation of rosin from the fats and its quantitative estimation has long been felt. To meet this need numerous methods have been proposed. Thus in Prescott's "Proximate Organic Analysis," p. 90, are recommended two, the first dependent on the treatment of the fat acids containing the rosin, with petroleum naphtha; the second, on the treatment of the same with a mixture of water and a nearly equal volume of alcohol. I have given these plans a careful trial, using for the purpose a mixture of known amounts of pure fat and pure rosin, but have found them wholly unreliable, as they fail to give even an approximate determination of the rosin known to be present.

A later and better method is found in "Spons' Encyclopedia," p. 1469, in which the rosin and fats are brought into the form of neutral soda salts. After a careful drying by evaporation, mixed with sand, these are digested in a mixture of absolute alcohol and ether, by which the resinate of soda is dissolved. But this method is very laborious, requiring at a later stage the use of a polariscope, and even then giving a result several per cent. from perfect accuracy, especially when the amount of rosin present is small.

The difficulty underlying the problem is the great similarity as regards solubility between oleic acid or its salts and the resins.

Every solvent for the one in the above schemes is to a considerable degree a solvent for the other. A systematic search has therefore been made for such a salt and such a solvent as shall serve to distinctly separate these two substances.

A plan of separation analogous to the separation of oleic acid from stearic and palmitic acids by digesting their lead salts in ether, thereby dissolving out the oleate of lead, has been investigated, and found to be entirely satisfactory both as regards accuracy and ease of execution.

The fatty salts of silver were found to be almost perfectly insoluble in ether, while the resinate of silver was found to be readily and abundantly soluble therein. A small percentage of alcohol does not affect the solubility of either, and for the sake of an advantage gained thereby was used in the course of experiments undertaken.

In applying this principle of separation, the silver salts of the three acids were at first precipitated from a perfectly neutral water solution of the potash salts by a neutral solution of silver nitrate. But the difficulty attending the filtering and washing of this precipitate, and the somewhat inaccurate results obtained, which were attributed partly to the decomposition of the silver salts from exposure during drying preparatory to treating with ether, caused its abandonment.

The following plan was finally adopted with success.

About 0.5 gram of the fat acids containing the rosin is introduced into a small flask. Twenty cubic centimetres of 95 per cent. alcohol are added, and the flask rotated till the fat acids and the rosin are dissolved. A drop of phenol phthalein is now added, and then a saturated solution of caustic potash in alcohol drop by drop, with thorough agitation after the addition of each drop, until the deep red color characteristic of alkalinity is obtained. One or two additional drops are now added, and the flask placed on a water-oven and kept at the temperature of boiling alcohol for ten minutes to ensure the saponification of the last portions of fat. The flask should be loosely corked. It is now cooled and the contents washed into a graduated 100 cc. cylinder by means of concentrated ether. The cylinder is filled with the ether exactly to the 100 cc. mark; then corked, best by a common cork twisted tightly in, and the contents mixed by a moment's shaking. About one gram of C. P. *neutral* silver nitrate is now rubbed to an impalpable powder in

a small mortar and then introduced into the cylinder. The latter is vigorously shaken for ten or fifteen minutes until the flocculent precipitate of silver stearate and oleate collects in the same manner as silver chloride upon shaking, and settles clear. Fifty to seventy cc. of the supernatant liquid are now syphoned off by means of a slender syphon, previously filled with ether, into a second 100 cc. cylinder, passing the liquid through a small filter paper if it is not perfectly clear. A small quantity of pulverized silver nitrate is shaken up with this to make certain that all the oleate and stearate are precipitated. If no flocculent precipitate appears this is the case. Twenty cc. of a mixture of hydrochloric acid and water, one-third the former and two-thirds the latter, are now added, and the cylinder vigorously shaken until the decomposition of all the silver salt present is complete. After the silver chloride has settled, an aliquot portion of the supernatant ether solution is syphoned off into a platinum dish and evaporated on the top of a water-oven to dryness. The residue is rosin containing a small amount of oleic acid, which can be accurately allowed for.

The following experiments will show the allowance to be made for the oleate of silver retained in solution, as well as the reliance which can be placed upon the process for accuracy.

Exp. I. One-half a gram of pure fat acid was treated according to the above plan, but with one-half the amount of alcohol and ether.

Forty cc. shaken with HCl and evaporated gave 0.0095 gram of residue. 10 cc. contain 0.00237 gram of oleic acid.

Exp. II. One-half a gram of pure fat acid was treated in the same way with full quantities of liquid.

Eighty cc. shaken with HCl and evaporated gave 0.0188 gram of residue; 10 cc. contain therefore 0.00235 gram of oleic acid. This very small and accurate correction of 0.00235 gram for every 10 cc. of liquid shaken up with HCl was applied in the subsequent experiments.

Exp. III. Some pure white castile soap was decomposed by acid. One-half a gram of the fat acids from the soap was added to 0.050 gram of common yellow rosin (colophony) and the whole treated as above. After corrections, 0.0497 gram on the whole quantity taken was obtained instead of 0.050 gram.

In order to ascertain whether the process would succeed with linseed oil, in which rosin is often to be determined, and also to test

the process when very small quantities of rosin are present, the following experiment was made.

Exp. IV. One-half a gram of the fat acids from linseed oil was added to 0.050 gram of rosin and treated as the above.

Seventy cc. shaken with HCl gave 0.0517 gram of residue. Subtracting the allowance for 70 cc., namely, 0.0164 gram, leaves 0.0353 gram or 0.0504 gram of rosin on the whole quantity taken instead of 0.050 gram taken.

As the principal value of the above process will be found in the estimation of rosin in soaps, of which it forms so frequent an adulterant, a number of experiments were made according to the above plan on the soap itself, dispensing with the preliminary decomposition of the soap in order to obtain the fat acids.

One gram of the soap in thin shavings is dissolved in the alcohol and treated in every way as above. Particular care is paid to the saponification as above directed, in order to make certain that no trace of unsaponified fat is left. This would pass through the remaining stages unchanged and increase the percentage of rosin. The results are so good and the process is so much simplified that this plan is recommended for commercial analysis. The determination of the percentage of fat acids is thereby avoided, and the time required for the process is shortened to a few hours. Pure soap free from rosin was used.

	Soap taken.	Rosin added.	Rosin found after correction.
Exp. V.	0.250 gram	0.0200 gram	0.0197 gram
Exp. VI.	1.000 "	0.0200 "	0.0209 "

Some experiments made by filtering the whole of the liquid instead of taking an aliquot portion as above did not give as accurate results, both on account of the difficulty of perfectly washing the flocculent precipitate, and the lesser degree of accuracy in making allowance for the oleate of silver dissolved.

Duplicate analyses of a cheap yellow soap known to contain rosin gave 29.00 per cent. and 29.30 per cent. of rosin present.

Some experiments to determine the applicability of the above process to the estimation of mineral oils and paraffin in the other fatty oils are contemplated, also a preliminary trial of a similar method of separating oleic acid from the other fat acids gives promise of accomplishing this with great accuracy.

Laboratory of Stillwell & Gladding, New York.

A NEW MANGANESE MINERAL.

By Malvern W. Iles.

In describing this mineral I have thought best to use the same general scheme of arrangement as that adopted in Dana's Mineralogy.

1. *Crystalline form.* The mineral is composed of loosely-adhering, very friable, thick orthorhombic (?) prisms, which are frequently found terminating in truncated pyramids.

2. *Hardness, etc.* (*a*) The mineral has a hardness of 0.75 to 1.0.

(*b*) The Jolly spring balance was used to determine the density. Great care was taken to obtain a very pure specimen, and sufficiently large for accuracy. The mineral was weighed in clear petroleum the density of which was 0.7975. The specific gravity was found to be 2.1627.

(*c*) Lustre: slightly glimmering, resembling pure kaolin, and a number of white efflorescent salts.

(*e*) Color: pure milky white, but sometimes stained with sesquioxide of iron.

3. *Chemical composition.* The mineral is to be classed under the general division *Hydrous Sulphates.*

A. Elements in the protoxide state.

(*e*) Epsomite group, containing iron, zinc and manganese.

The mineral under consideration very closely resembles Fauserite, which is a sulphate of manganese and magnesium, containing 40 per cent. of water of crystallization whose formula is

$$MgO.SO_3+2MnOSO_3+15HO.$$

The analyses of the manganese mineral under consideration lead to the formula

$$FeO.SO_3.ZnO.SO_3.5MnO.SO_3+28HO,$$

or, adopting the atomic weights now in use,

$$FeSO_4.ZnSO_4.5MnSO_4+28H_2O.$$

The results of a number of analyses are here given:

Residue, chiefly SiO_2.	ZnO.	FeO.	MnO.	HO.	SO_3.
0.54 per ct.	5.63 per ct.	4.12 per ct.	22.92 per ct.	29.88 per ct.	35.88 per ct.
0.75 "	6.23 "	3.73 "	21.78 "	32.54 "	35.84 "
0.60 "	..	4.18 "	21.92 "	29.94 "	35.93 "
..	..	4.55 "	22.06 "	31.44 "	36.20 "
..	..	..	..	32.14 "	36.11 "
..	..	..	..	32.78 "	35.77 "
..	..	.	..	31.82 "	35.85 "
..	..	..	..	30.58 "	..

Taking the average of all these results and correcting for the residue we have the figures given below. With them are also given the percentages required by the formula already stated:

Average results, corrected for residue.		Calc. for formula $ZnO.SO_3.FeO.SO_3.5MnO.SO_3+28HO$.
FeO	4.18 per ct.	4.58 per ct.
ZnO	5.97 "	5.15 "
MnO	22.31 "	22.58 "
SO_3	36.07 "	35.62 "
HO	31.60 "	32.06 "

The mineral has a bitter, astringent taste. It is very readily soluble even in cold water. The aqueous solution effervesces with sodium carbonate, and reddens blue litmus paper. Ammonium sulphocyanide does not give a test for sesquioxide of iron. Upon boiling the water solution, a very slight iron precipitate is formed.

Masses of the mineral, together with the gangue, were treated with pure distilled cold water, and, after digesting some minutes, the solution was filtered through double filter paper. The residue was then treated in a stream of water for a long time, thereby eliminating the lighter portions. The matrix was then dried and subjected to blow-pipe tests, which showed the presence of the sulphides of iron, lead and zinc. There were also detected manganese and some willemite. The gangue is a quartzose rock containing the above-named sulphides. On exposing the moist gangue, entirely freed from the soluble mineral, to the action of moisture and air, the mineral sulphides were found to become oxidized readily, giving strong reactions for sulphuric acid.

The filtrate was cautiously evaporated, a stream of hydrogen gas being passed through the liquid to prevent the oxidation of the

iron. Only by evaporating quite low were any crystals obtained, and then they were small unless great care was taken. I have succeeded in obtaining large, handsome crystals.

4. *Locality.* The mineral is found in Hall Valley, Park County, Colorado, upon the McDonnell mining property. This "claim" is near Middle Swan Creek, and 13 miles from Webster, situated on the Denver and Rio Grande R. R. The vein is located above timber line, the apex of location being in frozen snow. The gangue is over 300 feet wide, and shows upon the rocks this efflorescent salt. There is said to be a trace of gold and silver contained in the gangue for the above-mentioned entire distance. The gangue after being freed from the soluble mineral gave by fire assay at the office of the Grant Smelting Co. 9 ozs. silver per ton (2000 lbs.). In some places there is a pure streak of this mineral of 2 to 8 inches in width.

The McDonnell property has been developed by a tunnel 40 feet long, and has a shaft upon the claim 35 feet deep. During the excavations this mineral is brought to light. I am indebted to Mr. Frank Maloney for a description of the locality, etc.; also to Mr. Wm. R. Boggs, who gave me excellent samples for analysis. In conclusion, I will state that any parties may obtain samples for further scientific investigation by application to the writer. I have sent some of the best samples to Prof. Ira Remsen for more exact study and statements than I have made.

GRANT SMELTING CO., LEADVILLE, COLORADO.

ON THE SEPARATION AND DETERMINATION OF POTASH AND SODA BY THE INDIRECT METHOD IN PLANT ASHES, FERTILIZERS, AND SIMILAR SUBSTANCES.

BY CLIFFORD RICHARDSON.

Collier has shown[1] that with mixtures of pure chlorides of potassium and sodium, the indirect method is capable of furnishing very accurate results; but, in attempting to apply it to the determination

[1] Amer. Journal of Sci. 1864, 346.

of potash and soda in the ashes of plants, I have found that the usual manner of separating the mixed chlorides of the alkalies for subsequent determination of chlorine and calculation of the relative amounts of potassium and sodium, does not furnish them in a state of sufficient purity for the accuracy which this process requires.

Instead of the usual method of procedure, the following has been found to give the chlorides in perfectly pure condition. The impurities which are usually met with and resist removal are phosphoric acid and magnesia, and the latter can only be completely and easily displaced in the absence of all strong acids. For this reason the ash is dissolved in nitric acid and evaporated several times, to be sure of the conversion of chlorides to nitrates. It is then taken up with water and a few grams of oxalic acid added, and again evaporated once or twice on the steam-bath. The nitrates are in this way converted to oxalates, and, on gentle ignition, to carbonates. There then remain only phosphates, sulphates and carbonates. The residue is to be taken up with water and filtered through a filter as small as possible, removing as phosphate and sulphate of lime and as carbonate of lime and magnesia the greater part of these acids and bases. To the filtrate a slight excess of barium hydrate is added, and, after boiling and subsequent filtration, there remain in solution nothing but the alkalies as hydrates and the excess of barium. To insure complete freedom from magnesia, however, the filtrate is evaporated to dryness, much of the barium, as well as the alkalies, being at the same time converted to carbonates. The residue is treated with successive portions of water, not more than 5 cc. at a time, and filtered through a filter 7 cm. in diameter. To the filtrate, carbonate of ammonia, as free from empyreumatic matter as possible, is added, and after evaporation to dryness, to remove the excess, the residue is taken up with water again, and filtered through a small filter into a weighed platinum dish. This is to be covered with a watch-glass and the purest hydrochloric acid added, to convert the carbonates of the alkalies to chlorides. After evaporation and gentle ignition, a slight black carbonaceous residue will be found, which must be removed by filtration. The solution is then again evaporated, heated to 130° and weighed. The chlorides are quite pure, being clear white, and ready for the determination of chlorine.

This process has been in use for the past three years in the laboratory of the Department of Agriculture, and has given most satisfactory results.

The usual method with platinum has a tendency to throw all the error into an exaggeration of the amount of sodium present, especially if the mixed chlorides are impure; and in this way many of the older analyses show a percentage of sodium in the ashes of plants which most of my analyses, as carried out by this more careful method, do not confirm. For example, in the ashes of thirty-four grasses analyzed in 1878 sodium was found in only eighteen, and then in only two cases in amounts exceeding two per cent.; and in ten analyses of cereals sodium was found in none.

In fertilizer and soil analyses this method finds, also, a very convenient application.

WASHINGTON, D. C., *Oct.* 1881.

ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

XI.—ON THE CONDUCT OF NITRO-META-XYLENE TOWARDS OXIDIZING AGENTS.

BY IRA REMSEN AND M. KUHARA.

The experiments described in this paper were undertaken for the purpose of determining whether a nitro-group situated in the ortho-position with reference to an oxidizable residue in a benzene compound exerts a protective influence when the compound is subjected to the action of certain oxidizing agents. The influence of the sulphonic acid group and of its derivative, the sulphamide group (SO_2NH_2), has been determined in several cases, and the results have been recorded in earlier papers of this series. The question suggests itself, Does the nitro-group act like the sulpho-group? The facts thus far determined are not sufficient to warrant a satisfactory conclusion, though they make an affirmative answer appear probable, at least for such compounds as contain two oxidizable residues together with the nitro-group.

The particular case considered in this paper is that of the nitro-compound formed by treating metaxylene with nitric acid. It

was shown by Beilstein and Kreusler[1] that, when the nitro-compound or compounds obtained by treating ordinary xylene with nitric acid, are oxidized, only one of the methyl groups contained in the compound is changed to carboxyl, the product being a nitrotoluic acid. Commenting upon this fact, the authors say: "Offenbar bewirkt Eintritt negativer Elemente oder Radicale in den Kohlenwasserstoff dass derselbe widerstandsfähiger gegen Oxidationsmittel wird. Aehnliche Erscheinungen finden sich häufig." The orientation of the groups in the compound was not determined at the time. Later experiments proved that the compound is a derivative of metaxylene. Beilstein himself showed[2] that when the amido-metatoluic acid corresponding to the nitrotoluic acid above referred to is distilled with lime it yields ortho-toluidine. From these facts we may conclude that in the nitrotoluic acid the nitro-group and methyl-group are in the ortho-position relatively to each other, and that the carboxyl is in the meta-position relatively to the methyl. Whether the nitro-group is in the ortho- or the para- position relatively to the carboxyl cannot be decided without the aid of further experiments. It is known that when bromine acts upon metaxylene the orientation of the three groups in the product is expressed by the formula $C_6H_3.Br.CH_3.CH_3$ (1.2.4), and Wroblewsky[3] concluded that in nitrometaxylene the groups probably stand in the same relation to each other. Hence he gave to the compound the formula $C_6H_3.NO_2.CH_3.CH_3$ (1.2.4). This would lead to the formula $C_6H_3.NO_2.CH_3.CO_2H$ (1.2.4) for nitrometatoluic acid. Assuming this to be correct, the further conclusion is justified that, when nitrometaxylene is oxidized with chromic acid, the nitro-group protects the ortho-methyl group, while the para-methyl is converted into carboxyl. But the proof for the formula of nitrometaxylene can hardly be regarded as conclusive; and, further, as Beilstein's investigation was undertaken before it was known that ordinary commercial xylene is a mixture, it appeared possible that the nitrotoluic acid described by him might also be a mixture. It is hence plain that in order to reach positive conclusions the transformations above alluded to must be reinvestigated, and new experiments must determine the nature of the nitrotoluic acid from nitrometaxylene.

[1] Annalen der Chemie, **144**, 168.
[2] Zeitschrift f. Chemie, 1869, 524.
[3] Berichte der deutschen chemischen Gesellschaft, **9**, 497.

Preparation of Nitrometatoluic Acid.[1]

A large quantity of commercial xylene (from Kahlbaum's factory) which was found to consist mainly of the meta-variety, was boiled for a long time with dilute nitric acid, for the purpose of destroying, as far as possible, the para-xylene. The hydrocarbon left unacted upon was then distilled off with water-vapor, washed with ammonia, dried and rectified. It was found to be necessary to continue the boiling with nitric acid for from thirty to forty hours. The purified metaxylene was converted into the mononitro product, according to the method described by Beilstein and Kreusler.[2] Instead of distilling with water from a copper retort, we found it more convenient to distill from a large glass flask into which a constant current of steam was passed. The process can be carried on in this way without difficulty.

For the oxidation of the nitroxylene Beilstein and Kreusler[3] recommend the use of this mixture: 20 grams nitroxylene, 40 grams potassium pyrochromate, and 55 grams concentrated sulphuric acid diluted with twice its volume of water. As a considerable quantity of the nitroxylene escapes the action of the chromic acid when the above proportions are used, some experiments were made to determine whether the quantity could not be advantageously reduced. Further, as the time suggested for the oxidation is only six to eight hours, it was thought that by heating longer the yield might possibly be increased. It is unnecessary to describe our experiments in detail, as they all gave negative results, and only served to show that the first recommendations are really the best. Accordingly, in the preparation of nitrotoluic acid we have since followed closely the original directions. The yield is by no means satisfactory.

In order to determine whether, when nitroxylene is oxidized, the product is a single substance or a mixture, the acid precipitated from its solution in sodium carbonate was carefully washed and then converted into the calcium salt. The mother-liquor containing sodium carbonate was further evaporated, and all the acid which could be obtained from this was collected and examined. The calcium salt was easily obtained in crystallized form, and consisted

[1] The first experiments described in this paper were performed with great skill by Mr. Hermann Voorhees, one of the most promising young men I have ever had the good fortune to be associated with. His work was suddenly interrupted by a serious attack of illness, from which he soon afterward died. May these few words serve as a token of the respect and admiration felt for him by those who knew him here.—I. R.

[2] Annalen der Chemie, **144**, 167.

[3] *Loc. cit*

then of thin prisms radiating from a centre. By far the largest quantity of the salt was obtained in this form, while from the last mother-liquors there was deposited a less pure substance consisting of crystalline crusts. It was at first thought that this substance was a second salt. On being repeatedly recrystallized, however, it gradually assumed the form of the pure calcium salt first deposited. A very small quantity of material was obtained from the very last mother-liquors, which could not be purified by crystallization. Its quantity was too small to permit of a careful examination. The acid precipitated from it had nearly the same fusing-point as that precipitated from the pure salt; the fusing-point was, however, not constant. As, in the course of our examination we worked up about forty or fifty grams of nitrotoluic acid and obtained from this only a very minute quantity of an impure calcium salt from the last mother-liquors, the conclusion is justified that when nitroxylene is oxidized with chromic acid only one nitrotoluic acid is formed. Whether this is due to the fact that the nitroxylene itself is a single substance, or to the fact that only one constituent of the original mixture is capable of yielding an acid by oxidation, must for the present remain an open question.

The calcium salt above-mentioned was analyzed and gave these results:

I. 0.2023 gram salt lost 0.0169 gram H_2O at 150°; and gave 0.0627 gram $CaSO_4$.

II. 0.2713 gram salt lost 0.0211 gram H_2O at 185°; and gave 0.0848 gram $CaSO_4$.

	Calculated for formula $\left(C_6H_3\begin{cases}NO_2\\CH_3\\CO_2\end{cases}\right)_2Ca+2H_2O$.	Found. I.	Found. II.
Ca	9.17	9.12	9.19
H_2O	8.26	8.35	7.78

After the water of crystallization is driven off by heating to a high temperature, if the salt is allowed to stand in contact with the air it rapidly takes up one molecule of water. Even by standing in the balance-case, in which there was a good-sized vessel containing sulphuric acid, the salt absorbed one molecule of water in the course of a few hours. In two different specimens, which had been heated up to 180° and from which all the water was driven off, there were found respectively 4.68 per cent. and 4.68 per cent. water

after standing. The formula, $(C_6H_3NO_2.CH_3.CO_2)_2Ca+H_2O$, requires 4.31 per cent. H_2O.

The nitrotoluic acid precipitated from the calcium salt fused at 211° (uncorr.). On recrystallizing it from water, however, and then purifying it further by sublimation, the fusing-point was found to be 214° (uncorr.). The fusing-point of the acid precipitated from the calcium salt was not changed by repeated crystallizations of the salt.

Transformation of Amido-toluic Acid into Oxytoluic Acid.

Pure nitrotoluic acid was converted into amido-acid by treating it with strong hydrochloric acid and tin according to the directions of Beilstein and Kreusler. The amido-acid was easily obtained in pure condition, and was found to have the properties ascribed to it by its discoverers. They transformed a small quantity of the acid by means of Griess's reactions into the corresponding oxy-acid, but were unable to obtain the latter pure. In regard to it they say: "Wir erhielten die p-Oxytoluylsäure in Gestalt kleiner gelblicher Prismen. Die Säure ist in kaltem Wasser schwer, in heissem leicht löslich. Sie scheint ein Molecul Krystallwasser zu enthalten. . . . Die kleine Menge der erhaltenen Substanz erlaubte keine eingehenden Reinigungsversuche."

To obtain this oxy-acid in larger quantity and pure condition, a few grams of the amido-acid were dissolved in the smallest possible quantity of dilute nitric acid. A slow current of nitrous acid (from nitric acid and arsenic trioxide) was conducted into the well-cooled solution, when the diazo-compound was precipitated in the form of white crystals. After allowing the solution to stand for a short time until all the diazo-compound appeared to be deposited, the latter was rapidly filtered off through asbestus with the aid of an aspirator, and quickly dried by bringing it on unglazed porcelain. The pure dry substance was now brought into a large quantity of water and the solution boiled. A strong evolution of gas took place. When this ceased the solution was neutralized with ammonia. This caused the liquid to turn a dark brown color. It was evaporated to a small volume and acidified, when the oxy-acid was precipitated as a brown powder. It was dissolved in water and boiled with bone-black, by which all the color was removed, and, on concentrating the solution, the acid crystallized out.

The acid thus obtained crystallizes in fine, lustrous, silky needles. It is difficultly soluble in cold water, but easily in hot water. The solution is not colored by ferric chloride. It is easily soluble in cold alcohol and ether, but insoluble in bisulphide of carbon. It melts at 148.5°–149.5° (corrected). After drying at 100° it melts at 174° (corrected). It was analyzed with the following results:

I. 0.1682 gram air-dried acid lost 0.0097 gram H_2O at 130°.

			Calculated.	Found.
$C_8H_8O_3$	...	152	94.41	...
$\frac{1}{2}H_2O$	...	9	5.59	5.77

II. 0.1534 gram acid dried at 130° gave 0.3546 gram CO_2 and 0.0825 gram H_2O.

		Calculated.		Found.
C_8	...	96	63.16	63.03
H_8	...	8	5.26	5.97
O_3	...	48	31.58	...
		152	100.00	

The results agree, as will be seen, with those required by oxytoluic acid of the formula $C_6H_3\begin{cases}OH\\CH_3\\CO_2H\end{cases}+\frac{1}{2}H_2O$. The formula and all the properties of the acid indicate clearly that it is identical with the oxytoluic acid of Remsen and Iles,[1] obtained by them from sulphamine-metatoluic acid by fusing this with potassium hydroxide. The structure of the acid was shown to be $C_6H_3\begin{cases}OH(1)\\CH_3(2)\\CO_2H(4)\end{cases}$. The same acid was prepared by Tiemann and Schotten[2] by an entirely different method, which consisted in introducing the aldehyde group into ortho-cresole and oxidizing the aldehyde thus obtained. They called it ortho-homo-paroxybenzoic acid. The experiments of Tiemann and Schotten also lead to the conclusion that the structure of the acid is correctly represented by the above formula.

The experiments thus far described suffice to show positively that the structure of the nitrotoluic under investigation is that which was anticipated. As by simple, clean reactions we have

[1] Berichte der deutschen chemischen Gesellschaft, **11**, 888; and this Journal, **1**, 48, 114.
[2] Berichte der deutschen chemischen Gesellschaft, **11**, 767.

passed from the nitro-acid to an oxy-acid of the formula $C_6H_3\begin{cases}OH(1)\\CH_3(2)\\CO_2H(4)\end{cases}$ it follows that the orientation of the groups in the nitro-acid must be represented by the formula $C_6H_3\begin{cases}NO_2(1)\\CH_3(2)\\CO_2H(4)\end{cases}$

The conclusion is hence justified that the nitro-group in nitroxylene, being situated in the ortho-position relatively to one methyl-group and in the para-position to the other, protects the former from oxidation when the compound is treated with the chromic acid oxidizing mixture. This fact serves as a new illustration of the protective influence exerted by negative groups, to which attention was first called in this series of papers. It will be seen, further, that between the sulphonic acids of xylene and the nitro-product there is a close resemblance. When xylene is treated with sulphuric acid, the main product is a sulphonic acid of the same structure as the nitroxylene above considered. By oxidation and subsequent fusion with potassium hydroxide it is converted into the same oxy-acid as that obtained from nitro-xylene. There is, however, a second sulphonic acid formed, in which the sulpho-group is in the ortho-position relatively to both methyl-groups. By oxidation with chromic acid this disappears, and a single product corresponding to the principal sulphonic acid is obtained. Now, it may be that the original nitro-xylene is a mixture of two substances, analogous to the two sulphonic acids, and that only one of these yields an oxidation product, the other being destroyed.

The transformations above considered may be conveniently represented thus:

$C_6H_3\begin{cases}NO_2\\CH_3\\CH_3\end{cases}$	$C_6H_3\begin{cases}NO_2\\CH_3\\CO_2H\end{cases}$	$C_6H_3\begin{cases}NH_2\\CH_3\\CO_2H\end{cases}$	$C_6H_3\begin{cases}OH\\CH_3\\CO_2H\end{cases}$
Nitro-xylene.	Nitrotoluic Acid.	Amidotoluic Acid.	Ortho-homo-paroxybenzoic Acid.

Transformation of Amidotoluic Acid into Chlor- and Brom-meta-toluic Acids.

Chlortoluic Acid.—Some of the diazo-compound obtained from amidotoluic acid was boiled with concentrated hydrochloric acid. While boiling, a crystallized substance separated. It was purified

by boiling with bone-black and then crystallized from alcohol. It is almost insoluble in cold water, and but slightly in boiling. It is slightly soluble in cold alcohol, but quite easily in hot. It crystallizes from alcoholic solution in groups of nearly colorless fine needles. From a mixture of alcohol and water it is deposited in lustrous needles. It fuses at 204° (corrected), and sublimes easily. An estimation of chlorine was made by heating with lime.

0.1448 gram acid gave 0.1222 gram AgCl.

		Calculated for $C_8H_7ClO_2$.	Found.
Cl	...	20.82	20.85

The substance is a chlortoluic acid of the structure $C_6H_3\begin{cases}Cl(1)\\CH_3(2)\\CO_2H(4)\end{cases}$. It is identical with the so-called para-chlortoluic acid of Vollrath[1] obtained by the oxidation of chlorxylene with chromic acid. The above transformation furnishes the proof that when chlorxylene is oxidized, the chlorine atom which occupies the ortho-position relatively to one of the methyl-groups protects the latter from oxidation. The phenomena studied in connection with the nitro-product are repeated in connection with the chlorine-product.

Bromtoluic Acid.—This acid was prepared like that just described. While boiling, the product separated in the form of a crystalline powder. It was recrystallized from alcohol and obtained perfectly white. It is almost insoluble in cold and hot water. It is slightly soluble in cold alcohol, but quite easily in hot. It fuses at 205°–206° (uncorr.) or 208°–209° (corrected). A bromine determination was made with the following results:

0.25 gram air-dried acid gave 0.22317 gram AgBr.

		Calculated for $C_8H_7BrO_2$.	Found.
Br	...	37.2	37.98

The acid is $C_6H_3\begin{cases}Br(1)\\CH_3(2)\\CO_2H(4)\end{cases}$. Its properties are the same as those of the bromtoluic acid obtained by Fittig, Ahrens and Mattheides[2] by oxidizing bromxylene. There can be little doubt that the two are identical. Hence it is seen that when bromxylene is oxidized, the ortho-methyl-group is protected.

[1] Annalen der Chemie, **144**, 266.

[2] Annalen der Chemie, **147**, 32.

Although the above experiments prove conclusively that the substances examined are derivatives of metaxylene, it seemed desirable to transform the amido-acid into metatoluic acid. For this purpose the usual method of boiling with alcohol was employed. But instead of obtaining metatoluic acid, a well-crystallized acid, fusing, when purified, at 198°, was the result. This acid is insoluble in cold water, and only slightly in hot water. It crystallizes from an alcoholic solution. It is volatile with steam. It sublimes in light flakes. The analysis did not give satisfactory results. With the small quantity at our disposal it was impossible to determine what the acid is. Mr. P. H. Broun is at present engaged in preparing a larger quantity of it for the purpose of careful study, and in a short time the result of his examination will be made known.

Xylidine.—As we had in our possession a considerable quantity of nitroxylene, which was recovered from the oxidizing mixtures, it was thought best to examine this carefully for two purposes: (1) To determine whether this unoxidized material is the same nitroxylene as that which yields the nitrotoluic acid; and (2) whether it is a single substance or a mixture.

For the first purpose some of the product was treated again with the chromic acid mixture. The same nitrotoluic acid was obtained as in the first operation, and the quantity of the product was about the same. The nitroxylene recovered from this operation was again oxidized, and again yielded the same nitrotoluic acid. Hence it follows that this nitroxylene at least contains a considerable quantity of the substance which in the first oxidation yielded the nitrotoluic acid.

To determine whether the substance is a mixture or not it was transformed by means of tin and hydrochloric acid into the corresponding xylidine. After drying the xylidine it was treated with acetyl chloride and thus converted into the acetyl compound. By crystallizing from alcohol and water this was readily obtained in pure condition as very fine, lustrous needles. It dissolves readily in alcohol; is difficultly soluble in cold water, and not very easily in hot water. It fuses at 127°–128°. The properties are the same as those of the *a*-xylidine of Hofmann, the xylidine of Wroblewsky from metaxylene, and the *a*-xylidine obtained by Schmitz from *a*-amidomesitylenic acid. The experiments of Wroblewsky[1] and

[1] Berichte der deutschen chemischen Gesellschaft, 9, 497.

of Schmitz[1] have shown that the formula of this compound is $C_6H_3\begin{cases}NH_2(1)\\CH_3(2)\\CH_3(4)\end{cases}$, and our experiments confirm the formula. The nitroxylene used by us certainly consisted almost entirely of the one modification. The *α*-xylidine obtained from it was, as has been said, nearly pure. Some foreign substance contaminated it slightly; but, whatever the impurity may have been, its quantity was so small that it was impossible to separate it, and it was not sufficient to render inaccurate the statement that the nitroxylene recovered from the oxidizing mixtures is essentially a pure compound.

JANUARY, 1882.

REVIEWS AND REPORTS.

TRAITÉ DE CHIMIE GÉNÉRALE, COMPRENANT LES PRINCIPALES APPLICATIONS DE LA CHIMIE AUX SCIENCES BIOLOGIQUES ET AUX ARTS INDUSTRIELS: par PAUL SCHÜTZENBERGER, Professeur au Collège de France. 2 Vols. Paris. 1880.

Although more than a year has passed since this book appeared, no apology is necessary for calling special attention to it, even at this late day. Among the many text-books of chemistry that have been given to the public during the past few years, this one stands out prominently. It must be classed among the very best. The one characterizing feature of the book is objective treatment. The facts of chemistry are brought prominently forward, and the strictly logical conclusions which these facts warrant are then considered. There is an entire lack of the wild theorizing which plays such an important part in many inferior text-books of the last decade, and which has done so much to bring chemistry into disrepute. Many of these text-books are quite unintelligible to a chemist, not to say to the young student for whom they are intended. What conception can a writer have of the science of chemistry and the mental powers of students when at the outset of his presentation he discusses "types," "molecules," "equivalence," "atoms," "hydroxyl-groups," "structure," etc., etc.? Yet we need only pick up at random one of the recent books: the chances are that we shall

[1] Annalen der Chemie, 193, 177.

find these subjects taken up in the first twenty or thirty pages. If this is not so, then at least we shall find in some part of the book a chapter or two devoted to "theoretical chemistry," made up largely of dogmatic statements, which are sprung upon the reader without warning. Thus: "Nitryl (NO_2) is a negative compound radical"; "In sulphuric acid sulphur is a hexad, and there are two hydroxyl groups present in the acid"; "When to each of the bonds of a multivalent radical is united an atom of the same kind . . . the forces exerted at the several points appear to be . . . equal"; "The nitrogen atom has usually three bonds, although sometimes it has five"; etc. While these statements may be justified in some instances, if the facts upon which they are based are known, it certainly can do no good to make them without showing exactly how the facts lead to them.

From the kind of errors just referred to, the book in question is singularly free. In the introduction indeed the author clearly states his intention of keeping theory subject to facts. As, after a careful examination of the book, it seems to me that the author has admirably succeeded in doing what he intended to, I can not perhaps do better than to quote freely from his introduction.

In speaking of the changes in the views of chemists concerning the true nature of chemical phenomena, the author says: "The study of these changes teaches us how necessary it is to be distrustful and skeptical when we leave the domain of facts and enter that of hypothesis." . . . "Far be it from us to condemn the powerful efforts of thinkers who seek to utilize the vast material put at their disposal by their predecessors and increased by their own discoveries." . . . "Theory is not only useful, but even indispensable to the chemist; it is the beacon which guides him towards the unknown." . . . "But it is necessary to recognize and avow that the beacon is still dim and can only serve for short distances." On page iv. we read: "Without going farther, let us say at once . . . that between what is at present called the *atomic theory* . . . and the very old *hypothesis* of atoms and of discontinuous matter, there is only a very weak bond." The notion of atoms and of discontinuous matter is an hypothesis and nothing more.

"The atomic theory has its origin, on the contrary, in experiments. It is founded on facts fixed and undeniable, from which it is deduced by legitimate processes. It is *independent* of the hypothesis of atoms, and is connected with it only through a figurative language, and a nomenclature of which it would perhaps be well to rid itself.

"The chemical atom does not *necessarily* constitute a small indivisible mass, invariable in weight, form and volume. The chemical atom is for us only *the smallest ponderable quantity of an element which can take part in a reaction.* We regard this *smallest quantity* not as an absolute value, but as a relation; and if we fix it by a number, it is solely for the sake of comparison with the base of the system of notation adopted.

"Newton, in explaining the system of the moon by universal attraction, took care to add that things act *as if* masses mutually attract each other at a distance. In chemistry we can also say . . . : Things conduct themselves *as if* atoms or particles attract each other and unite to form complex molecules. But it is impossible for us to go farther and to admit that a particle of chlorine, for example, *really* possesses a special attractive force. . . These occult and special forces, which we are obliged to attribute to the atoms to explain each order of facts, are very little in harmony with the grand thought of the unity of the forces of nature. . . This unity should extend to chemical phenomena as well as to physical phenomena. The conquests of thermo-chemistry furnish proof positive that intimate relations exist between a chemical reaction and the manifestations of heat, of electricity and of light. . . The unity of the forces of nature is not merely a vague aspiration of the mind: it appears to us as a truth, and as one of the greatest conquests of science, founded as it is on transformation of the forces, demonstrated by experiments, both qualitative and quantitative. It gives great weight to the idea of the unity of matter of which it is the sister."

These quotations will serve to illustrate the spirit of the author as exhibited throughout the book.

The subject is taken up under three general heads: (1) GENERAL PHENOMENA; (2) ELEMENTS OR SIMPLE BODIES; (3) SPECIAL STUDY OF THE ELEMENTS. The first subdivision occupies something over a third of the first large volume, and is to the advanced student the most interesting part. The subjects of the seven chapters which make up this part of the book are: (I) *Object and aim of Chemistry—Definition of the general phenomena with which it has to deal;* (II) *Nomenclature and Symbols;* (III) *Physical character of bodies;* (IV) *Of Affinity and chemical phenomena in general;* (V) *Numerical laws and relations by weight according to which chemical combinations take place;* (VI) *Determination of Equivalents;* (VII) *Principles of Thermo-chemistry.*

It would lead too far to attempt to give an adequate idea of the author's method of treatment of the subject-matter under each of the heads above named. In general, it may be said that the subjects are treated more fully than is usual in text-books of chemistry, and the relations of the subjects to chemistry as a science are kept more clearly in view than is usual. Thus we find in chapter III. admirable treatment of the subjects of: The nature of gases; the diffusion of liquids or molecular diffusion; osmose; dialysis; and gaseous diffusion. The principal investigations to which we owe our present knowledge of these subjects are clearly described, so that the connection between what has been done in the way of experiments and the conclusions which are drawn is easily recognized; and the reader unconsciously becomes familiar with the methods of experiment which have been employed in each case. For an earnest

student of chemistry, who really desires to master the subject, I cannot think of a better exercise outside the laboratory than a careful reading of this book. The original papers, the results of which are discussed, should also be read; and as references to them are given in the proper places, the finding of these papers is facilitated.

The chapter on Affinity is of special interest. It opens with an historical review, in which the views of the earliest investigators are first given, and the changes in the prevailing views are clearly explained. The laws of Berthollet receive due attention. Speaking of the final overthrow of the electro-chemical theory of Berzelius, the author says: "In fact, the time has not yet arrived when we can seek to form an approximate idea of the cause of combination. This cause must be studied in its various manifestations before we become attached in too absolute a way to premature hypotheses. Without doubt, the mechanical theory of heat is destined to throw great light on the manifestations of chemical action; and, in the near future, we shall see chemistry become connected with the physical sciences by indissoluble bonds. I recall here the profound words pronounced at the Chemical Society of Paris by my illustrious master, M. Sainte-Claire Deville: 'Affinity, considered as a force, is an occult cause; if it is only the expression of a quality of matter, it ought to serve solely to designate the fact that such and such substances can combine under such and such well defined circumstances. All the investigations, all the tendencies of modern science, lead to the identification of the forces which act in the physical and chemical phenomena of nature. All numerical determinations tend to establish their equivalence. . . Affinity and cohesion cannot escape this identification, and already the mechanical theory unites them in a circle of arguments which ought soon to cause the disappearance of whatever they present that is vague and mysterious.'"

More than twenty pages are devoted to the interesting and important phenomena of dissociation. This is considered necessary because "dissociation has led chemists to modify to some extent their ideas concerning chemical action." The experiments of Sainte-Claire Deville are fully described, and everything that is of importance for an understanding of the phenomena is discussed.

The problem of determining atomic weights and equivalents is fully considered in chapter VI. The determination of equivalents is, in the first place, of course purely experimental, involving difficulties, to be sure, but not involving hypothesis. The object is to find "by analytical or synthetical methods, that is to say by means of the balance, the weights of the various elements which unite with a given weight of one of them taken as a term of comparison." There is, however, another thing to be done; that is, "to select, among the possible multiples which might be adopted, that one which agrees best with the analogies in the properties or with the accepted theoretical ideas." For the purpose of making this

selection, or, as we commonly say, for the purpose of determining the atomic weights, the author acknowledges the value of considerations based on the study of the phenomena of isomorphism, of specific gravity of vapors and of specific heat, and shows himself thus to be in harmony with the majority of chemists of the present day. His remarks on this subject in general are worthy of special notice. He is certainly not carried away by theories, nor does he go to the other extreme, as did St. Claire-Deville, and as Berthelot does now. Our author, a pupil of St. Claire-Deville, is evidently more inclined than his former teacher to acknowledge the value of some of the prominent views prevalent among chemists. And he justifies himself thus:

"We have thus far shown that simple relations exist between the numbers expressing the proportions by weight according to which bodies unite, react upon each other, are replaced one by another, and (1) the crystalline form, (2) the density in the form of gas, (3) the specific heat.

"Systems of equivalents or atomic weights might be established, satisfying either the conditions of isomorphism or those of the hypothesis of Avogadro, or again the law of Dulong and Petit. In the first case, the atomic weights would give similar formulas to all isomorphous bodies; in the second, all compounds would have equivalents or molecular weights corresponding to the same volume; finally, in the third place, the product of the specific heat of an element by its atomic weight would be equal to a constant. If the three systems thus established agree in the great majority of cases; if, further, the single system resulting from the three orders of phenomena does not meet with any serious contradiction in the facts of chemistry, there would be reason to adopt it with confidence, for it will be in entire harmony with the programme laid down above, with the greatest number of analogies. It is, in fact, this conclusion which we reach on taking all the known facts into consideration."

Again, p. 252, he says: "Attaching to the equivalent weights no hypothetical idea regarding the intimate constitution of matter, and taking no other guide in the choice of the numbers selected than the need of recalling and symbolizing the largest possible number of analogies, we are led to use the system most commonly employed at the present day in chemical text-books and memoirs—that which is known under the name of the *system of atomic weights.* It appears according to its designation to be based on the hypothesis of atoms. In reality it finds its strongest support in the facts and sums up in a satisfactory manner the principal results of experiment.

"As regards the atomic hypothesis itself, it should be considered merely as an image, a figurative comparison, intended to render more comprehensible and to emphasize the relations of the facts among themselves, to materialize, so to speak, the results of experiment; moreover, it is conducive to clear and precise language.

"The words atoms, molecules, mono- or polyvalent atoms, and all others of the prevalent nomenclature, correspond undeniably to experimental realities, and are deduced from important considerations, the fruit of long and brilliant investigations; but an unrestricted and absolute sense should not be attached to them."

This caution is undoubtedly in the interest of truth, for it is certainly of the highest importance that chemists should be able to recognize exactly where their knowledge of facts ceases and where the products of speculation begin to appear. No matter how perfectly the hypothesis may be in accordance with the facts, we must not forget that it is hypothesis.

Chapter VII. is devoted to the principles of thermo-chemistry. Here again we have the same clear and satisfactory treatment. In the space of fifteen pages the phenomena of thermo-chemistry, the methods of investigation, and the results achieved by Thomsen and Berthelot, are very satisfactorily explained. Referring to the fundamental principle of thermo-chemistry, that "the heat evolved or absorbed during a chemical transformation . . is the tangible representative of the molecular work accomplished during the change of state, and is equivalent to the loss or gain of energy experienced by a system of bodies reacting upon each other," the author says, page 256: "The preceding principle is nothing but that of equivalence of heat and work applied to molecular mechanics.

"M. Thomsen expressed similar ideas in 1853, although in terms less in harmony with the theories now in vogue. In *Die Grundzüge eines thermochemischen Systems*, he says: 'The total heat developed in a reaction is a measure of the loss of chemical force resulting from the act of combination. For the same body and the same temperature, the intensity of chemical force is constant.' Replacing the words *intensity of chemical force* by *energy*, we substitute a precise meaning for a vague and badly defined idea. This criticism, however, takes away nothing essential from the important conclusions drawn by Thomsen from his statement.

"M. Deville had very nearly the same idea concerning affinity as that expressed by Thomsen. He used the expression *latent heat* instead of energy. Lavoisier and Laplace admitted that the decomposition of a body into its elements absorbs as much heat as the combination of the elements had produced. . . The calorimetric experiments of Andrews, of Hess, of Th. Woods, of Favre and Silbermann, and the more recent ones of M. Berthelot and M. Thomsen, all tend to verify this direct consequence of the application of the mechanical theory to chemistry."

While in the parts of the book already referred to the best opportunity is given for originality of treatment, the remaining portions will by no means be found to be conventional. In nearly every chapter something will be found which is worthy of special study, and which is not commonly met with even in advanced textbooks.

In the chapter on the Physical Properties of the Elements the most important contributions to spectroscopy are considered. M. Salet's methods of observing the spectra of vapors and gases; Masson's apparatus for observing the spectra of metals; Lecoq de Boisbaudran's burner for spectroscopic work; the same chemist's apparatus for observing the spectra of sparks; the tube of Delachanel and Mermet for spectroscopic observations, are all carefully described, and the descriptions are rendered clear by excellent woodcuts.

Passing on to Book Third, which has to deal with the special study of the elements, the interest is kept up, for we find a great many facts emphasized which are usually not mentioned at all, or, if mentioned, only in such a way as to lead the student to think that they are of very little importance. Special care is taken in devising experiments to illustrate the important physical properties of substances. A number of the experiments described are original, and others are new to chemical text-books.

While fully impressed with the paramount importance of the purely scientific side of his subject, the author does not lose sight of, or undervalue, the practical questions which present themselves. The methods used for manufacturing chlorine and oxygen on the large scale; for extracting sulphur from its ores; a new apparatus for the refining of sulphur; the apparatus for refining phosphorus; an apparatus for the manufacture of bone-black, and many other methods and forms of apparatus are very fully described and illustrated.

But I have perhaps said enough to awaken interest in the book among those who may read this notice. That is all I desire. I believe that the tendency of the book is excellent, and, though undoubtedly many things might be pointed out in regard to which there may be two opinions, and other matters might be censured, I am sure that the book is freer from errors of judgment and of execution than is usually the case. I believe that the author's method of presenting the subject is the right one, and that if most of our teachers could become imbued with his spirit, we should have less crudeness of thought among our young men—and old, for that matter. In learning chemistry we want first a solid foundation of facts, such as a conscientious student of this book might acquire from it. Afterwards we are ready to consider the speculations which are suggested by these facts. The facts should, of course, be presented in proper form, so that their relations may be easily recognized, and not merely enumerated as if they were totally disconnected. The opposite method is, however, much in vogue. With a very inadequate presentation of facts a mass of theoretical matter is involved, and the importance of the latter is often unduly magnified. The result is that the student, never having clearly recognized the actual connection between the facts and the speculations, and being fascinated by the various hypotheses which he has learned, but which he does not fully comprehend, makes un-

warranted use of them. We see the effects in many of the papers which appear in the chemical journals of to-day. Many of these would never have been written if the writers had ever learned to look at chemical phenomena purely objectively. I. R.

LEHRBUCH DER ORGANISCHEN CHEMIE ODER DER CHEMIE DER KOHLENSTOFFVERBINDUNGEN: von DR. AUG. KEKULÉ, Professor der Chemie an der Universität zu Bonn. Fortgesetzt unter Mitwirkung von DR. R. ANSCHÜTZ, Privatdocent in Bonn, und DR. G. SCHULTZ, Privatdocent in Strassburg. Dritter Band. Dritte Lieferung.

The sudden appearance of some old friend who has not been heard from for thirteen years, and who has consequently been given up for lost, could not occasion more surprise than did the unexpected appearance of a new number of Kekulé's great treatise on organic chemistry. The last number published in 1867 was the first one of the third volume; then, in 1880, came the second number. Now we have the third, and, though we cannot quite get over a feeling of uncertainty, and the fear that our erratic friend may again leave us in the lurch, it behooves us in the meantime to be thankful for what we get, and to take courage from the brief notice with which Professor Kekulé reintroduces his work. He says: "As my occupation leaves me even now very little time for literary labor, I have considered it necessary to call in younger forces, and I believe that I have found efficient coöperators in Dr. Anschütz, of Bonn, and Dr. Schultz, of Strassburg. The assistance of these gentlemen is secured for the future, so that rapid progress of the work may be promised with confidence."

This book has had a curious history in some respects. The time occupied in writing it was necessarily so great that the author changed his views regarding some important matters more than once before the end of the second volume was reached. If a student should attempt to work through it now without being fairly familiar with the history of chemistry during the past fifteen years, he would certainly be much mystified at times. This fact, however, scarcely diminishes its value. For an advanced student it is nearly as valuable to-day as the day it first appeared. The grasp of the author is shown on every page. No man without a very vigorous and broad mind could have written such a book. And no doubt it has exerted a powerful influence on the progress of chemistry. It is suggestive throughout. Much of the work which has been done in Germany during the past twelve or fifteen years owes its incentive to Kekulé's Organic Chemistry. It may be that, as Kolbe so persistently claims, a great deal of this work is bad, but it must not be forgotten that a great deal is good; and in order to get good work we must always have a fair proportion of that which is bad, no matter under what influence it is done, or what may be the guiding hypothesis.

But it is both too late and too early to pass judgment on Kekulé's book as a whole. Too late, if the intention is merely to call attention to it, for every chemist knows it well. Too early, if the object is to determine exactly the character of the influence which it has exerted on the progress of chemistry: that must be left to the future historian of the science. It is, however, justifiable to express a doubt whether the parts of the book which are still to appear will come up to the standard of the old parts. This depends to a great extent upon the amount of editorial work which the nominal author does upon it. It is possible to conceive of such a division of labor between Professor Kekulé and his coworkers that all the matter collected should be digested by the chief and then presented by him after it had undergone this process. We might under such circumstances get a product which would be worthy of Professor Kekulé. But, as he himself says in his brief introductory note, he has very little time for literary labor, so that plainly the ideal arrangement is an impossibility. What we shall probably get will be a very excellent handbook of organic chemistry, accurate in details and presented in clear form; but this will not be a continuation of *Kekulé's* book. Kekulé will be left out; and it was after all the Kekulé in it that made it so valuable and so popular. The prophecy may be somewhat premature, but an examination of the numbers at hand seems to justify it. I. R.

Report on Progress in Physiological Chemistry.

[*Continued from page 366.*]

Gastric Digestion and the Products formed.

Chemical Nature of Peptones.—Although there has been, particularly of late, considerable work done upon this important subject, it has not as yet led to a complete agreement of opinion. In fact, the numerous results which have been recorded within the last five years have been so strikingly at variance with each other, that the theories of the chemical nature of peptones have been from time to time variously modified. This is probably in part explained by the great diversity of conditions under which the experiments have been conducted; conditions which, though slight in themselves, no doubt play an important part in determining the nature and composition of the products formed. Thus Herth calls attention, in the artificial preparation of peptones, to the fact that by long-continued digestion the products formed are liable to differ somewhat from those obtained in the case of rapid digestion (4–6 hours), and speaks in favor of the latter method as more analogous to what takes place in the body normally. The difficulty attending the preparation of a chemically pure peptone

by artificial digestion is more dependent upon the great liability of not completely removing syntonin than upon the presence of fats and other possible extractives. The removal of syntonin from a digestive fluid, by neutralization of the acid, offers two difficulties: first, the propensity of the peptones to form with different metals salt-like combinations which, unfortunately, are not constant in composition, as is noticeably the case when solutions of calcium or barium hydroxides are used for the neutralization of the acid; and, secondly, the difficulty of obtaining a *complete* neutralization when sodium carbonate is used, which, while it diminishes the inorganic impurities of the peptones, renders extremely difficult the complete removal of the unaltered albumin. When, however, from the method of preparation, barium or calcium chloride is present in the peptones, recourse is generally had to repeated precipitation and digestion with alcohol, which, however, fails to completely remove the salts. Again, it has been suggested to separate the baryta from peptones by careful addition of sulphuric acid, the liberated hydrochloric acid being removed in its turn by moist silver oxide, a method, however, which does not yield uniform results, owing probably to the oxidizing action of the silver oxide.

In the preparation of pure peptone, Herth,[1] who worked under the guidance of Maly of Graz, employs phosphoric acid, which, according to Gorup-Besanez, works only one-tenth as actively as hydrochloric acid. For proteid material he uses coagulated albumin from fresh eggs, and as ferment a pepsin solution made according to the method of Krasilnikoff[2] and Brücke, and purified by dialysis. The method, which is detailed as follows, is characteristic of the means adopted by many workers on this subject to obtain chemically pure products without reference to the physiological conditions normally present in the digestive process: Coagulated albumin from sixty eggs is digested for 24 hours in 1 per cent. phosphoric acid for the complete removal of inorganic salts, then thoroughly pressed and finally extracted with boiling water; the purified product is then heated at 40° C. with 4 litres of .65 per cent. phosphoric acid, to which 40 cc. of the clear pepsin solution have been added. At the end of five hours the entire mass of albumin is almost completely dissolved, although the digestions are usually continued somewhat longer. When the digestions are finished the phosphoric acid and syntonin are removed by the addition of freshly-precipitated and thoroughly-washed lead carbonate; this being added until the clear yellow fluid shows itself exactly neutral to litmus. The small quantity of lead contained in the filtrate is removed by hydrogen sulphide. The fluid is then concentrated on the water-bath and finally precipitated with strong alcohol. The so-prepared peptones are digested with alcohol, finally dissolved and reprecipitated, this operation being repeated three times.

[1] Robert Herth, Zeitschrift f. physiolog. Chem. 1, 277.
[2] Krasilnikoff: Hoppe-Seyler's med. chem. Untersuch. p. 241, 1867.

Peptones prepared in this manner are pure white; heated over sulphuric acid for several hours at 100° C. they lose from 4 to 6 per cent. of water, and at this temperature become brown in color. Their aqueous solutions react exactly neutral, and in every other respect their reactions agree with those noticed by other late observers. Particularly noticeable was the unlimited solubility of the peptones in water, which character was not changed by long soaking in alcohol, nor even by long-continued boiling in alcohol.

By a study of the reactions of his peptones with different precipitants, Herth disagrees with Adamkiewicz[1] when he says that "peptones possess the same precipitability with the important chemical reagents as albumin." According to Herth, the peptones do form, even with the heavy metals, the same compounds as albumin, most of which, however, are soluble, while the albumin compounds are insoluble. For analysis the peptones were dried at 100–105° C. till of constant weight. A portion dried at 100° C. in an atmosphere of hydrogen showed no essential difference on analysis.

	Albumin. (Wurtz.)	Albumin peptone. (Herth.)	Fibrin. (Maly.)[3]	Fibrin peptone. (Maly.)
C	52.9	52.60	52.51	51.40
H	7.2	7.12	6.98	6.95
N	15.7	16.80	17.34	17.13
Ash		1.00		

Taking the analysis of albumin by Wurtz as an average result, although the nitrogen is undoubtedly too low from the method of determination, it is seen that there is but little difference in composition between the albumin and the peptone formed from it. On the other hand, there is a noticeable difference in composition between the albumin-peptone of Herth and the fibrin-peptone of Maly.

Herth has also made a large number of analyses of peptones prepared by fractional precipitation with alcohol and ether, and, from his closely-agreeing results, decides on the individuality of the peptones, and that there are no grounds for belief in the theory of peptones being a mixture of several closely-related bodies, as has been sometimes suggested.

Adamkiewicz[4] concludes from his study of peptones that chemically they are nothing but albuminates, which differ from ordinary albumin by containing a diminished content of inorganic salts and a somewhat different molecular formation. Adamkiewicz's view is mainly based on Lehman's analysis of blood-fibrin, which contained 2.17 per cent. of ash. This theory has been contradicted by various authorities, particularly by Maly and Herth, both of whom found the quantity of salts only slightly, if at all, dimin-

[1] Die Natur und der Nährwerth des Peptons, 1877.
[2] De la Nature et du Role physiologique des Peptones, 1878.
[3] Pflügers Archiv. **20**, 329.
[4] *Loc. cit.*

ished when pure albumin was employed in the preparation of the peptone. Again, Kistiakowsky[1] has found only .65 per cent. of ash in pure fibrin, while Adamkiewicz's peptones contain 1.16 per cent. of ash. Undoubtedly the quantity of salt is simply dependent upon the manner of preparation of the peptone; the purer we obtain the albumin or peptone the freer it is from ash. But perhaps the most striking proof of the falsity of Adamkiewicz's views is shown by Aronstein's oft-quoted experiments. He found that while albumin, deprived of its salts, was as non-coagulable by heat as a solution of peptones, addition of salts to such a solution of albumin restored its coagulability, while the peptone solution under like treatment was unaltered. Thus the most striking feature of peptones, viz. their non-coagulability, is wholly independent of inorganic salts.

Herth concludes that the analytical data give no idea of the actual alterations which albumin undergoes in its transformation into peptone, and thinks it possible that a rearrangement of the atoms takes place, a different grouping in the albumin molecule through the process of peptone formation. The belief in the possibility of an inner alteration of the albumin with a simplifying of the molecule, whereby, as in the case of peptone, a greater solubility, diffusibility, etc., are obtained without changing the percentage composition, has had but few supporters. Herth, however, quotes in favor of this view the fact that paraldehyde $(CH_2O)_3$, which, in the ordinary condition is solid and insoluble in water, is volatilized by heat, and shows a vapor-density agreeing with the formula CH_2O, ordinary aldehyde; even heating with water is sufficient in some cases to bring about a decomposition of complicated molecules, thereby leading to solubility in water exactly as in the case of heating albumin with water. Thus Herth is inclined to compare the change of albumin to a disgregation of the molecular compounds, or, in other words, to look upon the formation of peptones as the simple solution of polymeric bodies.

In opposition to the theory of Adamkiewicz and that of Herth, Henninger[2] has, in a long and able investigation, studied the properties and composition of various peptones, compared the results with the composition of the original proteid, and advanced the theory advocated by Wurtz and Hoppe-Seyler, that the formation of peptones is due to a process of hydration. The following figures represent his average analytical results:

	Fibrin peptone. (Henninger.)	Fibrin. (Maly.)	Albumin peptone. (Henninger.)	Albumin. (Wurtz.)	Casein peptone. (Henninger.)	Casein. (Dumas & Cahours.)
C	51.58	52.51	52.31	52.90	52.13	53.50
H	7.02	6.98	7.05	7.20	6.98	7.05
N	16.66	17.34	16.38	15.70	16.14	15.77
Ash	0.31	...	0.51	...	1.15	...

[1] Pflügers Archiv. 9, 438. [2] De la Nature et du Role physiologique des Peptones, 1878.

It is evident from these analyses, which do not differ materially from those of Maly and Herth, that the peptones, while they approach in composition the original proteid, contain regularly a diminished amount of carbon (0.5–1 per cent.), a difference altogether beyond the errors of analysis. Hydrogen and nitrogen, however, are not materially different in the two classes of compounds, a fact which is easily reconciled with the theory of hydration which Henninger adopts as the true explanation of the formation of peptones. The formula of albumin established by Lieberkühn is $C_{72}H_{112}N_{18}O_{22}S$, which would give to albumin the molecular weight of 1612. Supposing, now, the formation of peptones to be a simple process of hydration, the addition of one molecule of water, viz. 18, would increase the percentage amount of hydrogen only to a very insignificant extent, about .05. On the other hand, the content of carbon would be diminished in the neighborhood of .5 per cent., while that of nitrogen would be decreased .18 per cent. It thus becomes very apparent that the elementary analysis of peptones cannot be expected by itself to absolutely prove the hydration hypothesis. Adopting the results of Schützenberger's[1] late work on the constitution of albumin, and assuming 4800 to represent more correctly the molecular weight, a diminution of 1 per cent. in the proportion of carbon would suppose an addition of six molecules of water in the process of hydration. Thus, while the analytical data tend to corroborate the hydration hypothesis as the true explanation of the transformation of proteid matter into peptones, many other facts tend to make this the more plausible theory; for we well know that peptones are formed under the influence of agents which produce hydration; thus, boiling water, the action of dilute acids, and lastly ferments, the nature of which is to decompose by hydration; all of which facts tend to substantiate the hydration theory.

Not satisfied with this, however, Henninger[2] has attempted to produce albumin again from his peptones by a process of *dehydration*. This he partially succeeded in doing, by heating a mixture of 10 parts of dry peptones with 25 parts of glacial acetic acid at 80°C. for one hour. The acid fluid was then distilled until the greater part of the acid was removed. The residue was dissolved in a little water, and subjected to dialysis for the complete removal of the acid. The clear solution remaining possessed the following characters:

1. It is coagulated by heat, the precipitate being insoluble in a small quantity of nitric acid.
2. It gives, with nitric acid, a white precipitate, soluble in a large excess.
3. It is completely precipitated by acetic acid and potassium ferrocyanide.
4. It is completely precipitated by careful addition of potassium hydroxide, the precipitate being redissolved by a slight excess.

[1] This Journal, **2**, 207-210. [2] *Loc. cit.* p. 53.

5. It is precipitated by solutions of the neutral salts, sodium sulphate, potassium nitrate, etc., the precipitates being readily dissolved by an excess of acetic acid.

It is thus very evident that the product formed is syntonin, the next modification of albumin.

This very important result has received confirmation from Hofmeister,[1] who, working on gelatin, discovered that pure gelatin, by repeated drying at 130°C., passes completely into a substance which possesses all the chemical properties of collagen. Led by this reaction, he tried a similar experiment with peptones, and obtained a corresponding result. If dried fibrin-peptone is heated for several hours at 140°C., or a shorter time at 160-170°C., it becomes changed in part, under browning and evolution of alkaline vapors, into a substance similar to albumin. Cold water dissolves a great part of the substance, while a flocculent residue remains which shows all the reactions of freshly precipitated albumin. This, then, seems to establish on a firm basis the theory that peptones are simply proteid bodies modified by hydration. Kossel[2] has analyzed the chlorine- and calcium compounds of fibrin-peptones, and has found the free peptones to possess a somewhat different composition from that already stated. His results, calculated for the free peptones, are as follows:

C	H	N	S	O
48.97	7.06	15.14	1.16	27.67

These results, which differ widely from those of Maly,[3] Henninger and others, can be explained according to the views of the author in several ways: first, the free peptones when dried at 110° C. possibly give up water which exists in chemical combination, while the peptone compounds retain it when dried at the same temperature. Maly[4] however looks upon the inorganic constituents of Kossel's peptone compound (2.34 per cent. chlorine and 5.68 per cent. calcium) as mere impurities, though Kossel purified his product by repeated precipitation with alcohol, in which free calcium chloride is readily soluble. Maly then argues that if such is the fact, the average composition of Kossel's peptone would be changed to C51.51.H7.13 and N15.95 per cent. which indeed does not materially differ from the results of Maly, Henninger and others. Again, it is possible that the compounds analyzed by Kossel are the results of a further hydration, whereby compounds with a smaller content of carbon would naturally be formed. This seems the more probable, since the peptones of Maly and Henninger particularly were the products of a weak digestive action, while those of Kossel were formed by 24 hours' digestion at 38° C., with an active gastric juice containing .4 per cent. fuming hydrochloric acid.

[1] Zeitschrift f. physiolog. Chem. **2**, 206.
[2] Zeitschrift f. physiolog. Chem. **3**, 58. Pflügers Archiv. **13**, 309.
[3] Pflügers Archiv. **9**, 585; **20**, 315. [4] Pflügers Archiv. **20**, 325.

These results again suggest the possibility that peptones are a mixture of several isomorphous bodies. Maly[1] holds to the opinion that there is only *one* principal product of digestion, only one peptone, which differs but slightly from the mother-substance in composition, and that, therefore, peptones are not a product of the *splitting-up* of albumin. Kossel, however, finds in his work evidence that the composition of the peptone is in part dependent on the activity of the pepsin digestion, the product first formed being by further hydration changed to another body of somewhat different composition. Thus Kossel is inclined to the belief that more than one peptone can originate from a single albumin, and that those bodies which we now term peptones do not actually possess a chemical individuality. This view would accord with Kühne's[2] discoveries in regard to the two kinds of peptones, which he distinguished by the names *hemi-* and *anti-*; and although no chemical analysis has yet been made of these two bodies, which differ so far as is known only in their behavior to trypsin, still it is more than probable that two bodies which differ so widely in their mode of decomposition differ also more or less in composition. Again, Kossel[3] well remarks that if only one peptone is formed by digestion, in fractional precipitation, the more soluble portion would not differ in composition from the remaining fractions. A study of the composition of Maly's[4] fractional alcohol precipitates indicates that his product is a mixture of several bodies. Herth's results,[5] obtained by fractional lead precipitations, would seem to indicate the same thing, viz. that from albumin several bodies originate; but this result must be accepted with some modification, as it has been shown that the lead acetate is capable of working a decomposition. By a comparison of Maly's and Kossel's preparations it is noticeable, as regards the percentage of carbon, that under Maly's figures are differences which are greater than the difference between his lowest figure and Kossel's highest.

Maly's		Kossel's	
3d fraction.	2d fraction.	2d fraction.	1st fraction.
52.33	50.80	49.69	48.98
1.53		1.11	0.71

As regards the nature of peptone, whether it is an acid, base, or both, the preponderance of evidence is on the side of its being an acid, though capable of acting both as an acid and a base. Lehman originally ascribed to peptones acid properties. Recently, however, Kossel has formed combinations of peptones with acids. This view of the acid character of peptone has also been confirmed by Henninger,[6] who likewise prepared compounds of peptone with sulphuric, hydrochloric and nitric acids. He considers them as feeble amido-acids, and as such are capable of acting either as

[1] *Loc. cit.*
[2] This Journal, **2**, 210.
[3] Pflügers Archiv. **21**, 183.
[4] Pflügers Archiv. **9**, 585.
[5] Zeitschrift f. physiolog. Chem. **1**, 289.
[6] *Loc. cit.* 43-44, also Comptes rendu, **86**, 1415.

acids or bases. Thus by the addition of baryta water to an aqueous solution of peptone, an alkaline solution is obtained, from which carbonic acid will precipitate a portion of the base, while barium *peptonate* remains in solution and can be precipitated by alcohol.

The combination of peptone with acids is formed directly whenever an acid is added to a solution of peptone. Thus if peptones are dissolved in glacial acetic acid, and then sulphuric, nitric or hydrochloric acid be added, an abundant white precipitate is immediately formed, which settles at once as a viscous mass to the bottom of the dish. This compound is a salt of the peptone corresponding to the acid employed. It is entirely soluble in water, yielding a colorless solution. Peptones also combine with salts, such as calcium chloride, phosphates, etc., all of which are insoluble in alcohol. By dialysis the greater part of the salt is removed, as its osmotic power is greater than that of the peptone itself. This fact well illustrates the loose union existing between the peptone and the salt.

Propeptone.—When fibrin is subjected to pepsin digestion, several bodies other than true peptones are formed. Among these is one which of late has attracted considerable attention. Several years ago Kühne called attention to a peculiar albuminous body formed during digestion, which he named hemialbumose.[1] Since then Schmidt-Mülheim[2] has written considerable concerning a body which he terms propeptone, evidently identical with Kühne's hemialbumose. Recently Salkowski[3] has called attention to the fact that when fibrin is digested with pepsin for a few hours only, a solution is obtained which, on neutralization and concentration, gives the well-known reactions with acetic acid and potassium ferrocyanide, with acetic acid and sodium chloride, and with nitric acid, indicating the presence of what Meissner terms *a*-peptones. All three of these reactions, however, disappear on heating, but return again as the solutions become cool. The reactions, then, are not due to albumin, for this must necessarily be precipitated by heat. When such a gastric digestion is continued for 1–2 days, then these reactions are not obtained; the intermediate prôduct has been wholly transformed into peptone proper. This fact may perhaps throw some light on the difference in composition noticed between peptones which result from a long-continued and active digestion, and those which are formed by shorter digestions with weaker but perhaps purer digestive fluids. This intermediate pro-

References to other recent investigations on the chemical nature of peptones:—C. A. Peckelharing: Zur Kenntniss des Peptones, Pflügers Archiv. **22**, 185. A contradiction by Maly of a portion of this investigator's work is contained in Jahresbericht d. Thierchemie für 1880, 31. A. Danilewsky: Ueber den Hydrationsvorgang bei der Peptonisation, Centralbl. f. d. med. Wiss. 1880, **42**. Weiteres über das Peptone. C. A. Peckelharing, Pflügers Archiv. **26**, 515, 1882.

[1] This Journal, **2**, 211.

[2] Zur Richtigstellung der Geschichte Propeptons, Virchow's Archiv. **81**, 575. Weitere Beiträge zur Kenntniss des Propeptons, Jahresber. d. Thierchemie für 1880, 23.

[3] E. Salkowski, Virchow's Archiv. **81**, 552.

duct, which Salkowski recognizes as Kühne's hemialbumose, can be prepared in some quantity as follows: 50 grams of commercial *peptonum siccum* are poured into 500 cc. 1 per cent. sodium chloride solution, and heated on the water-bath. The slightly turbid fluid is then acidified with acetic acid and boiled, whereby some albumin is generally precipitated. The filtrate, after cooling, is treated with powdered salt in sufficient quantity to have a portion remain undissolved (about 37.5 grams to 100 cc. fluid), and the mixture shaken vigorously. Almost immediately a light, somewhat tenacious precipitate settles out, which is washed with salt solution. The pressed precipitate is then dissolved in 300 cc. warm water, when the proteid body is again precipitated by the addition of an excess of salt to the strongly acidified solution. This second precipitate of hemialbumose, with considerable salt, is then dialyzed until the outer fluid gives only a slight or no reaction with silver nitrate. The filtered inner fluid is then concentrated, and the hemialbumose precipitated by the addition of an excess of absolute alcohol.

The so-prepared substance is a snow-white powder, free from ash and soluble in warm water. A 5 per cent. solution shows the following characteristic reactions:

1. Heated to boiling, it is not coagulated.

2. Pure nitric acid gives a precipitate which, by warming, dissolves with an intense yellow color. The precipitate reappears on cooling.

3. It gives precipitates with acetic acid and potassium ferrocyanide, with Millon's reagent, and yields the biuret reaction.

The substance rotates the plane of polarized light to the left, a 5 per cent. solution having for white light a specific rotary power of 78–80°. When heated at 140° for 14 hours the hemialbumose becomes insoluble, hardly dissolving at all even in boiling water.

It thus becomes plain that in an artificial as well as in a physiological pepsin digestion at least three well-defined products can be separated: 1. The so-called neutralization precipitate, syntonin or antialbumose[1] of Kühne; 2. Hemialbumose or propeptone precipitated by sodium chloride; 3. Peptone proper or true peptones, including both the hemi- and antipeptones of Kühne. In a long-continued or very active digestion, the first and second products are further changed into the true peptones. Thus it is more than probable that in many cases products which have been studied as true peptones, notably in the case of Adamkiewicz, have been in reality a mixture of these three bodies in varying proportions depending on the activity of the digestive fluid. It yet remains to be proved whether the so-called true peptone is a mixture or a chemical individual, for at present there is not sufficient evidence to warrant a decisive conclusion. Undoubtedly the true peptones

[1] See this Journal, **2**, 211.

may undergo further hydration or partial decomposition by long-continued digestion, since it is well known that the pancreatic ferment changes a part of its peptones into crystalline decomposition products. It would not be strange then if gastric peptones, even though they possess at some period in their formation a chemical individuality, should by further digestion undergo a partial decomposition.

R. H. CHITTENDEN.

(*To be continued.*)

THE RELATIONS BETWEEN THE PHYSICAL PROPERTIES OF ORGANIC BODIES AND THEIR CHEMICAL CONSTITUTION.

Under this title J. W. BRÜHL gives an account of a large number of observations recently made by him, the object of which was to show what relation, if any, exists between the chemical constitution and the thermal phenomena of liquid carbon compounds. The full memoir has appeared in volume II of the *Monatshefte für Chemie*, p. 716. The author has, however, furnished a good abstract which is published in the *Berichte der deutschen chemischen Gesellschaft*, 14, 2533, and from this the following account is mainly taken.

The previous investigations[1] of the author have shown that a simple relation exists between the refractive power and the constitution of liquid carbon compounds. It has also been found that simple relations exist between the constitution and the density, the boiling point, the rate of transpiration, and probably also of the specific volume. To use his own words: "This correlation of the various physical manifestations of organic compounds induced me to compare also their thermal and optical properties with each other, and led me to the discovery of a very simple connection between the refractive power and the heat of combustion of these bodies.

"I. It was first found that, if oxidation of the bodies be effected in successive stages, the changes exert the same influence on the optical as on the thermal properties. The refractive power $\frac{A-1}{d}$ of a body is decreased as the body unites with more and more oxygen; the more oxygen enters into the compound, the less the refractive power becomes, just as the heat of combustion is also decreased by this process. The abstraction of hydrogen or the replacement by oxygen produces the same result, so that the refractive power as well as the heat of combustion of the hydrocarbons is greater than that of equal weights of all the bodies which are formed by oxidation of the hydrocarbons, as the corresponding alcohols, aldehydes,

[1] This Journal, 2, 352.

acids, oxyacids, etc. The differences between the thermal and optical constants of adjoining members of an oxidation series decrease with increasing molecular weight, when the bodies have analogous structures. Thus these differences are smaller between propyl alcohol and propyl aldehyde, than between ethyl alcohol and acetic aldehyde, etc.

"II. The influence of the introduction of the halogens in the optical and thermal constants is analogous to that of oxidation. The specific refractive power and the specific heat of combustion, *i. e.* that of equal weights of the bodies, become the smaller the more chlorine atoms enter. . . .

"III. In the homologous series of alcohols, acids and esters, the refractive power and the heat of combustion increase as the number of carbon atoms increases, while the differences for the increment CH_2 decrease with increasing molecular weight in the case of both constants.

"IV. I had previously proved that the refractive power of isomeric bodies of the same degree of saturation is the same, and hence independent of the structure. Substances of one and the same class, and the same molecular formula, as, for example, isomeric alcohols, aldehydes, acids, etc., are hence, as regards their optical properties, identical. The latest investigations of Louguinine, Berthelot and others have shown that isomeric bodies of analogous chemical character evolve the same quantities of heat when burned.

"V. The relation between the refractive power and the heat of combustion holds good also for polymeric substances. The constants of the polymerisation products are in both cases smaller than those of the mother-substances. . . .

"VI. Isomeric bodies of unequal degrees of saturation have unequal refractive power. I proved that bodies which contain doubly linked atoms have greater refractive power than isomeric bodies in which this kind of linking does not occur. It was shown further, that the refractive power of such bodies as contain doubly linked carbon atoms is greater than that of bodies which contain carbon and oxygen doubly linked together. The general correlation in the optical and thermal conduct of bodies made it appear probable that the influence of double linkage of the atoms would extend to the heat of combustion of the bodies. This assumption is confirmed by the latest observations of Louguinine.

"These showed, first, that the heat of combustion of bodies in which doubly linked carbon atoms occur is greater than that of isomeric bodies, in which this kind of linkage is not found, but in which double linkage of oxygen and carbon is present.

"Thus the unsaturated alcohols evolve more heat than the isomeric aldehydes or ketones, and this accords with the optical conduct of these bodies. Allyl alcohol, for example, whose refractive power is greater than that of propyl aldehyde and of acetone, also evolves more heat when burned than these substances.

"VII. The phenomenon, that the double linkage of atoms which increases the refractive power of bodies, also increases their heat of combustion, throws light on the nature of this kind of atomic union.

"When two substances of the same molecular formula evolve unequal quantities of heat on combustion, the cause can only lie in the different energy of these compounds. Hence by the above results we are led to the conclusion that the energy of substances in which double linkage of atoms occurs is greater than the energy of isomeric substances in which such double linkage is lacking."

The fact that the unsaturated compounds have greater energy than the saturated, indicates that the atoms are not as intimately associated in them as in the saturated compounds; or, to state the conclusion in the author's words: "*It follows that the so-called double linkage of atoms in reality represents not a stronger, but a weaker attraction than the simple linkage. The assumption of a stronger or closer union of the atoms, of a double linkage between them, in unsaturated bodies, is hence in direct opposition to facts.*"

"This result is also partly confirmed by investigations on the specific volume. The well-known labors of Kopp and of Buff showed that the supposed doubly linked atoms require more space than those that are singly linked. This is easily understood if, in accordance with the above reasoning, we assume that the so-called double union does not correspond to a more intimate, but rather to a weaker connection of the atoms. For it appears then quite natural that the specific volume of atoms should be greater, *i. e.* that they should be farther removed from each other, the more loosely they are connected. If, however, we assume, as heretofore, that the unsaturated atoms are more intimately or doubly united, it is not clear why they should be farther removed from each other than those which are more weakly or singly united.

"This reasoning finds farther support in the rule discovered by Kekulé that in the oxidation of bodies with so-called double linkage of carbon atoms, the splitting of the molecule takes place just where this double linking is supposed to exist.

"The greater 'disgregation' of unsaturated compounds, and the fact that their molecules occupy relatively greater space, may be indicated in their structural formulas by representing the distance between unsaturated atoms as greater than that between the saturated. Thus, for example, we might express the connection of the atoms in allyl alcohol and propyl aldehyde by the following formulas:

$CH_2 \ldots CH\text{–}CH_2.OH$
Allyl alcohol.

$CH_3\text{–}CH_2\text{–}CH \ldots O.$
Propyl aldehyde."

On the Specific Viscosity of Liquids and its Relation to their Chemical Constitution.

Graham several years ago recognized that a connection exists between the chemical constitution of various liquids and the time of their transpiration through capillary tubes. Rellstab and Guerout subsequently investigated several liquids with reference to this property. The most thorough investigation of the subject has recently been made by Richard Pribram and Al. Handl. The capillary tube, which contained the liquid examined, was immersed in a larger tube filled with water, kept at a constant temperature. The authors employ for the specific viscosity (Zähigkeit) the expression

$$z = \frac{t.\ 100}{t_w},$$

where t represents the time of transpiration of the liquid considered, and t_w the time of transpiration of an equal volume of water through the same capillary tube.

It was proved by earlier investigators that in homologous series the time of transpiration of liquids increases with the molecular weights. The more recent results of Pribram and Handl confirm this conclusion, and show further that in homologous series the specific viscosity of liquids, at elevated temperatures, increases by a constant. The following tables contain the specific viscosity of three classes of homologous liquids as determined by them:

	$z_{50°C.}$		Difference.
Isoprophyl chloride	16		
Isobutyl "	19	...	3
Issamyl "	22	...	3
Nitroethane	29		
Normalnitropropane	34·5	...	5·5
Normalnitrobutane	39	...	4·5
Propionic acid	45		
Normalbutyric acid	57	...	12
Valeric acid	71.5	...	14.5

In aldehydes and ketones, compounds which contain dissimilar atoms joined by double union, the specific viscosity is considerably less than in the corresponding alcohols where single union prevails. A single example will make this evident:

	$z_{10°C}$	Difference.
Propylalcohol	175	
Propylaldehyde	26.5	148.5

No generalization is made concerning the effect of double union between carbon atoms upon the specific viscosity of organic compounds. In some instances unsaturated compounds, that is, compounds in which double union is supposed to exist, have a lower specific viscosity than the corresponding saturated compounds; while the reverse is frequently the case.

Guerout, relying upon his observations, stated that isomeric esters have the same time of transpiration for equal volumes. Pribram and Handl have determined the specific viscosity of a large number of isomeric esters. Their results show that Guerout's statement is wrong. From the compounds examined by them, "the ester containing the normal radical shows a greater viscosity than the ester isomeric with it, and this holds true whether the isomerism occurs in the acid or alcohol radical." This is equally true of the aldehydes, propyl alcohol (at 50°), nitropropanes, butyric acids and butyric iodides.—(*Sitzungsberichte der Wiener Akademie der Wissenschaften*, **78**, 52; **80**, 17; and *Monatshefte für Chemie*, 1881, 643.)

C. P.

NOTES.

Concerning Morphine.

The only facts hitherto known concerning the constitution of morphine, $C_{17}H_{19}NO_3$, are that, of the three oxygen atoms contained in it, two are associated with hydrogen, forming two hydroxyl groups, and the third is a "bridging" or ketone oxygen atom. It has also been considered that morphine contains a pyridine nucleus, for by distillation with caustic potassa a small quantity of pyridine was obtained. E. v. GERICHTEN and HUGO SCHRÖTTER have recently subjected morphine to distillation with zinc dust. In addition to the usual products, the distillate contained the hydrocarbon phenanthrene and a base which is believed to be phenanthrene-chinoline ($C_{17}H_{11}N$). The quantity of the base obtained was, however, insufficient for its thorough examination, but it seems highly probable that morphine is a derivative of phenanthrene, to which phenanthrene-chinoline is probably very closely related.—(*Annalen der Chemie*, **210**, 396.)

On New Elements and their Position in the Natural System.

D. MENDELEJEFF has recently published some remarks of interest, an abstract of which is given in the *Berichte der deutschen chemischen Gesellschaft*, **14**, 2821. A translation of the abstract is here given.

Of the many newly discovered metals of cerite and gadolinite, only two in addition to the well-known cerium, lanthanun, didymium

and yttrium, can be regarded as established elements. These are scandium and ytterbium. As scandium corresponds perfectly to the ekabor the discovery of which was foretold by Mendelejeff, its position in the periodic system of the elements was also determined before its discovery. Ytterbium finds a place in accordance with its properties, if the atomic weight of Nilson, 173, be accepted, and the oxide be represented by the formula Y_2O_3.

Mendelejeff gives the periodic system of the elements the following form, which he has adopted in the fourth edition of his *Principles of Chemistry*, now appearing:

			I.		II.		III.		IV.		V.		VI.	
R_2O	I		Li	7	K	39	Rb	85	Cs	133	..		..	
RO	II		Be	9	Ca	40	Sr	87	Ba	137	..		..	
R_2O_3	III		B	11	Sc	44	Y	89	La	138	Yb	173	..	
RO_2	IV	(H_4C)	C	12	Ti	48	Zr	90	Ce	142	..		Th	231
R_2O_5	V	(H_3N)	N	14	V	51	Nb	94	Di	146	Ta	182	..	
RO_3	VI	(H_2O)	O	16	Cr	52	Mo	96	..		W	184	U	240
R_2O_7	VII	(HF)	F	19	Mn	55	..		..		..		..	
RO_4					Fe	56	Ru	103	..		Os	?192	..	
	VIII				Co	58	Rh	104	..		Ir	193	..	
					Ni	59	Pd	106	..		Pt	195	..	
R_2O	I	H 1	Na	23	Cu	63	Ag	108	..		Au	196	..	
RO	II		Mg	24	Zn	65	Cd	112	..		Hg	200	..	
R_2O_3	III		Al	27	Ga	69	In	113	..		Tl	204	..	
RO_2	IV	(H_4R)	Si	28	??	72	Sn	118	..		Pb	206	..	
R_2O_5	V	(H_3R)	P	31	As	75	Sb	120	..		Bi	209	..	
RO_3	VI	(H_2R)	S	32	Se	79	Te	?125	..		..		.	
R_2O_7	VII	(HR)	Cl	35.5	Br	80	I	127	..		..		..	

All the more carefully investigated cerite and gadolinite metals find appropriate places in the system, and there is at present no good reason for changing it as Nilson and Petterson desire to. Using this system as a guide we can, for example, predict the existence of ekamanganese, whose atomic weight will be about 100, and which will yield colored compounds and a whole series of oxides corresponding to the oxides of manganese. The changes in the atomic weights of cerium, yttrium and other elements, proposed by Mendelejeff in 1870, on the basis of his periodic law, have been shown by later investigations to be justified. The position of beryllium cannot be changed to the third or fourth group, as the decrease in the atomic heat in the series Li, Be, B, C is analogous to that in the series Na, Mg, Al, Si. The three following important conditions appear not to have been sufficiently considered in the examination of the cerite and gadolinite metals: 1. The investigation of the higher oxides, particularly in the presence of alkalies and energetic oxidizing agents; 2. the possible existence of basic salts; 3. the possibility of the formation of meta-compounds the existence of which in the case of thorium has been proved.

Nicotinic Acid from Pyridine.

Laiblin has recently shown that nicotinic acid is a derivative of pyridine, the two being related the same as benzene and benzoic acid. He tried to prepare the acid from pyridine by means of ethyl chlorcarbonate, but did not succeed. O. FISCHER has now by another method passed from pyridine to nicotinic acid. He first made a pyridinesulphonic acid by heating with pure concentrated sulphuric acid for a long time at 320–330°. The sodium salt of the sulphonic acid was then distilled with potassium cyanide, and the cyanide thus obtained treated with hydrochloric acid at 110–120°. The acid obtained was found to be identical with nicotinic acid.—(*Ber. deutsch. chem. Gesell.* **15**, 62.)

Caesium and Rubidium.

CARL SETTERBERG has made a careful study of some new caesium and rubidium compounds, and has succeeded in preparing metallic caesium from the chloride by means of electrolysis. The material was obtained by working up residues from the preparation of lithium compounds from lepidolite. Tons of this material were at his disposal. The separation of pure salts was effected as follows: Three to four hundredweight of the impure alums (the residues just mentioned) were dissolved in enough water to make a solution of 20° *Beaumé* when boiling. The deposit from this solution contains all the rubidium and caesium compounds. This operation is repeated until the potassium alum is removed. Then the crystallization is continued and rubidium alum obtained in pure condition. Finally, the caesium alum is obtained. Thinking that possibly other alkaline metals might be contained in the mixture, the crystallization of the caesium alum was continued until only a very small quantity remained. No evidence of the presence of new metals was obtained. The author prepared in the course of two weeks 40 kilograms of rubidium alum and 10 kilograms of caesium alum. Rubidium was prepared by distilling, after carbonizing, 1500 kg. rubidium ditartrate, 150 kg. calcium carbonate and the necessary quantity of sugar. The operation was in every respect satisfactory. The attempt to prepare metallic caesium by reduction of the carbonate with charcoal was not successful. By electrolysis of caesium cyanide, however, the metal was obtained, though only in small quantity. It was found better to use a mixture of 4 parts caesium cyanide to 1 part barium cyanide instead of pure caesium cyanide. Caesium is very similar to the other alkali metals. It floats on water, and acts like potassium and rubidium as regards the accompanying phenomena. It takes fire quickly in the air.—(*Annalen der Chemie*, **211**, 100.)

Obituary Notes.

JOHN W. DRAPER, M. D., LL. D., Professor of Chemistry and Physiology in the University of New York, died January 4,

1882, in his 71st year. He was born in England, but came to this country at the age of 22. He took his medical degree at the University of Pennsylvania, and was appointed almost immediately to the professorship of chemistry and physiology in Hampden Sidney College, Virginia. Soon afterwards he was appointed professor in the University of New York, and remained actively connected with that institution to the time of his death. He was widely known as an investigator and writer. Many papers written by him appeared in the American Journal of Science, the Journal of the Franklin Institute, the American Journal of Medical Science, and in the London Philosophical Magazine.

JOHN STENHOUSE, a well-known English chemist, died recently at the age of 70. He studied under Thomson and Graham in Glasgow and afterwards under Liebig in Giessen. In 1851 he was appointed to the chair of chemistry in the Bartholomew Hospital, London. He suffered a stroke of paralysis and remained permanently crippled for a number of years, and his eyes became so affected that his time was necessarily spent in a dark room. Notwithstanding these great disadvantages, Stenhouse continued at intervals to prosecute his favorite researches, especially in the field of organic chemistry, until his death.

THÉOPHILE JULES PELOUZE, born February 11, 1807, in Velouze, a scholar of Gay-Lussac and an intimate friend of Liebig, was professor of chemistry in Paris. Together with Frémy he wrote the "Chimie générale," and published a number of important memoirs on chemical subjects. He died March 4, in Paris.

RUDOLPH BÖTTGER, born in 1806, teacher of chemistry and physics at Frankfort, died April 29, at the age of 75. Though, like Schönbein, he never used a balance, his numerous discoveries were of the highest importance. Among the substances the discovery of which is due to him, may be mentioned gun cotton, collodion, safety matches. The latest and, for different branches of industry, extremely important discovery of Böttger's was that of nickel-plating oxidizable metals.

FRANZ VON UCHATIUS, the well-known discoverer of Uchatius steel and steel bronze, born in 1811 in Thereseinfeld, died June 5, 1881.

ETIENNE-HENRI SAINTE-CLAIRE DEVILLE, the eminent French chemist, was born at St. Thomas on the 11th of March, 1818. He came to Paris as a boy, and a love for chemistry was developed in him, particularly by the lectures of Dumas. At the age of 33 he was appointed professor in the "École normale superiéure" in Paris. To the public he is known through his investigations on the manufacturing of aluminium, while his numerous

memoirs, especially in the field of inorganic chemistry, have made his name immortal among chemists. Among his many discoveries may be mentioned nitric anhydride, boron (conjointly with Wöhler). His investigations on the phenomena of dissociation are classical. Deville also made successful experiments on the preparation of artificial gems. He died at Boulogne, July 1, 1881.

WILHELM WEITH was born in 1846 at Homburg. He was professor of chemistry in the University and the Polytechnic school at Zürich. He published a large number of papers on subjects from the field of organic chemistry. He died November 29, 1881.

ALEXANDER POPOFF, professor of chemistry in Warschau, died August 18, 1881. He is well known through a series of investigations pertaining to certain oxidation phenomena presented by organic compounds.

To the Editor of the American Chemical Journal:

SIR:—There appeared in your October number for this year a review of my Manual of Sugar Analysis, by Dr. C. Fahlberg, from which I quote: "Although caustic lime is mentioned as influencing the rotatory power of cane-sugar, it is not stated how calcium sucrate and other sucrates have to be treated in order to obtain correct results with the polariscope." I wish to point out, that in two places in the above mentioned work I have given the necessary directions for meeting this difficulty in the polariscopic test, *i. e.* by slight supersaturation of the alkali with acetic or phosphoric acids—first on page 176, and again on page 252, under the head of cane-sugar estimation in the chapter on the analysis of molasses and syrups, to which section there are also several cross-references.

Very respectfully,

Philadelphia, Dec. 27, 1881. J. H. TUCKER.